FINAL TECHNICAL REPORT

Project Title:	High Selectivity Oxygen Delignification

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Project Objective: The overall objective of this program was to develop improved extended oxygen delignification (EOD) technologies for current U.S. pulp mill operations. This was accomplished by:
♦ Identifying pulping conditions that optimize O and OO performance;
♦ Identifying structural features of lignin that enhance reactivity towards EOD of high kappa pulps;
♦ Identifying factors minimizing carbohydrate degradation and improve pulp strength of EOD high kappa pulps;
♦ Developing a simple, reproducible method of quantifying yield gains from EOD;
♦ Developing process conditions that significantly reduce the capital requirements of EOD while optimizing the yield benefits.

Chapter I. Background:

The production value-added bleached kraft pulp has seen a renaissance in bleaching technologies over the past decade. A brief review of the literature indicates that the bleaching revolution of the last decade has dramatically changed kraft pulping and

bleaching technologies. As summarized by Singh,[1] pulp bleaching operations in the early part of the past millennium were primarily centered on chlorine. Changes in environmental regulations and societal pressures have dramatically altered the bleaching landscape. The early 1990's saw two competing bleaching technologies; a variety of researchers proposed the replacement of chlorine with Totally Chlorine Free (TCF) bleaching chemicals (i.e., Z, P, A, etc.) whereas Elemental Chlorine Free (ECF) was championed by many others.[2,3,4] In the U.S.A., EPA's promulgated Cluster Rules[5] approved the use of ECF bleaching technologies, while other parts of the globe saw increased industrial application of TCF bleaching technologies.

In the late 1990's, several research groups began to publish articles documenting problems in achieving high brightness and brightness stability for TCF bleached pulps. A study by Chirat and La Chapelle[6] examined the brightness stability of softwood and hardwood kraft and bisulfite industrial pulps subjected to ECF and TCF bleaching sequences and then exposed to heat or light. Based on these studies, the authors concluded that TCF bleached pulps generally experience higher brightness reversion upon heat or light exposure than do ECF pulps. The pulp ketone content was shown to negatively influence brightness stability upon heat exposure and even more so if aldehyde groups in C1 or C6 positions were present. In addition, for a given degree of brightness reversion, light exposure results in lower pulp degradation than heat exposure, which suggests separate mechanisms at work. Other researchers have supported the overall reversion trends of ECF and TCF pulps.[7]

Of equal importance were the reported differences in strength properties of ECF and TCF bleached pulps. A recent article by Sjostrom[8] examined the strength properties of pine and birch kraft pulps that were bleached with sequences containing peracetic acid, performic acid, Caro's acid or chlorine dioxide. The chemical, fiber and paper properties of the pulps were determined after each bleaching stage in order to find out in which stage differences between the pulps appear. According to these results, the bonding and strength properties of unbeaten ECF bleached pulps were higher than those of TCF bleached pulps. The TCF pine pulps were very similar to each other, whereas the TCF(Pfa) birch pulp differed from the other pulps in having lower strength. The TCF(Pfa) pulps also had lower surface lignin contents than the other pulps studied. In both pine and birch pulps, higher paper strength properties could be obtained with high carboxyl group content, but the carboxyl group content alone could not explain the differences between the pulps. On the other hand, the ECF pulps had both longer fibers and fewer fiber deformations, which could partly explain their higher strength. After beating for 2000 revs in a PFI mill, the strength properties of the TCF pulps were inferior to those of the ECF pulp. In the case of the pine pulp, this was probably due to the higher zero-span strength and the better bonding properties of the ECF fibers, while the difference between the birch pulps was mainly in the bonding properties. Bleaching to 85% brightness instead of 89%, by using less peracid in bleaching, brought the strength properties closer to those of the ECF pulp, but the same level could not be reached. Studies by Seisto et al.[9] came to the same conclusion as Sjostrom. Lumiainen[10] employed an industrial-scale refining technique on a series of eleven ECF and seven TCF bleached Scandinavian softwood kraft pulps to determine the refining behavior of chlorine-free

pulps. Compared to chlorine bleached pulps, the ECF pulps had slightly lower brightness and required significantly more refining energy. Although it was necessary to refine the ECF pulps to slightly higher freeness values, the pulps exhibited strength properties comparable to those of chlorine-bleached pulps. The TCF pulps were significantly lower in brightness than chlorine bleached pulps and required more refining energy. The TCF pulps required refining to significantly higher freeness values and exhibited lower strength properties than either the ECF or chlorine-bleached pulps. Regardless of whether ECF and TCF bleaching technologies are employed oxygen delignification is a key component in both approaches.

Improving the overall economics of pulping and bleaching operations while simultaneously remaining in compliance with this nation's environmental regulations is an important goal for the pulp and paper industry.[11] Oxygen delignification is one of the most promising technologies available to achieve this goal by utilizing the enhanced selectivity of oxygen delignification over extended kraft pulping to low lignin content pulps. Recently, extended oxygen delignification (EOD) processes have been developed that improve the typical delignification effects of an O-stage from ca. 50% to 70%. Mill results from 2-stage oxygen delignification have demonstrated the potential of this technology. Interestingly, it appears that EOD operates best when the temperature of the first stage is relatively low (ca. 85°C) with a high charge of alkali and oxygen applied. The second O stage then functions principally as a high temperature extraction stage. Following the above principals, the SCA mill in Ostrand Sweden is able to delignify a softwood kraft from kappa # 26 to 9 with excellent strength properties. Lab and select mill trials have shown that EOD of high kappa kraft pulp can improve overall pulp yields by 1 to 4% and could provide a pay-back in 16–26 months.[12]

Fundamental studies have shown that oxygen delignification occurs principally by oxidizing free phenolics in lignin. Remarkably, studies by Moe et al.,[13] Senior et al.,[14] and Gellerstedt et al.[15] have all shown that less than 50% of the phenolic sites of lignin are consumed during an O or OO-stage. These results suggest that the both the O and EOD technologies are operating far from optimal lignin degradation conditions and a tremendous opportunity exists for improving these stages. Our knowledge of the fundamental processes contributing to the degradation of carbohydrates and how to minimize these reactions is even less understood. Future advances in oxygen delignification of high kappa pulps for improved yield capabilities will require an increased understanding of:
♦ How pulping influences the bleachability of an O or OO-stage;
♦ The kinetics of oxygen delignification of high lignin content pulps as a function of NaOH charge, O_2 concentration, temperature, consistency (medium or high) and additives (role of $MgSO_4$);
♦ The factors controlling lignin, hemicellulose, and cellulose degradation during EOD;
♦ Development of a yield sensor for mill applications of EOD technology.
This research program was directed at addressing these issues. A key consideration of this program was if and how to best integrate kraft pulping operations with oxygen delignification. This knowledge was projected to be a key asset to improve the overall bleach pulp production and physical properties.

I. Review of Kraft Pulping:

In 2001, the world chemical pulp production was over 180 million metric tons. The United States produced 53 million metric tons; 85 percent of this was from chemical pulping. The kraft pulping process is the most commonly used chemical pulping process, accounting for 98 percent of chemical pulp production in the United States and 92 percent of chemical pulp production in the world.[16] Although in use since 1879, the kraft pulping process remains the dominant commercial pulping process today. One major reason for its predominance is that the kraft process produces stronger pulps than any other pulping process. In addition, it is insensitive to the presence of bark and high amounts of extractives and has been found to be adaptable to both hardwood and softwood tree species. The kraft process requires shorter cooking times than other chemical pulping processes. Finally, efficient recovery of pulping chemicals and the production of heat and valuable materials from by-products such as tall oil and turpentine from pine species has been a strong asset to the kraft pulping process. However, there are several disadvantages to kraft pulping which include high capital investments, high reaction temperatures, low pulp yields, odor generation by degradation products, and the dark color of the resulting pulps.

During the kraft pulping process, wood chips are treated with a mixture of sodium sulfide and sodium hydroxide, also known as white liquor, at elevated temperatures to produce a pulp suitable for the manufacture of paper and related products.[17] The temperature in the digester is increased to approximately 170°C for roughly two hours, depending on the degree of delignification desired. The hydroxide and hydrosulfide anions react with lignin during this treatment, causing the polymer to fragment into smaller alkali/water soluble fragments. The sulfide accelerates the pulping process; therefore, the wood chips are exposed to high temperatures and alkaline conditions for a shorter period of time than in other alkaline pulping processes like the soda process, thereby producing a pulp that is much stronger than soda pulp.[17,18]

Kraft delignification occurs by modifying the structure of lignin in two different ways to enhance its dissolution. The first is to degrade the lignin into smaller units by cleaving interunit linkages. The second is to introduce hydrophilic groups into the polymer and cleaved fragments, making the lignin more soluble in the cooking liquor. These phenomena occur when linkages holding the phenylpropane units together are cleaved, thereby generating free phenolic hydroxyl groups. The presence of these hydroxyl groups increases the hydrophilicity of the lignin and lignin fragments. Thus, the solubility of the lignin in the cooking liquor is increased. Meanwhile, the carbon-carbon linkages, being more stable, tend to survive the kraft pulping process.[19]

There are three fairly distinct phases of delignification during kraft pulping which include the initial phase, bulk phase, and residual or final phase. The three idealized phases of delignification are shown in Figure I.1.[19] The initial phase of delignification, taking place at temperatures below 150°C, has been characterized as a rather unspecific alkaline extraction leading to the dissolution of approximately 15-20% lignin and 20-25% of the

carbohydrates present in the wood. The delignification rate during this phase is first order with respect to lignin concentration and independent of the hydroxide and hydrosulfide ion concentrations, provided minimum threshold amounts of these ions are used. The activation energy of the initial delignification (61 kJ/mol) indicates that the rate of the process is diffusion controlled rather than chemically controlled. As the cook proceeds above 150°C, the bulk phase of delignification begins. The bulk phase includes the heating period from 150°C to 170°C and the cooking treatment at 170°C, and this phase results in the dissolution of the main portion (about 60%) of the lignin present in wood.
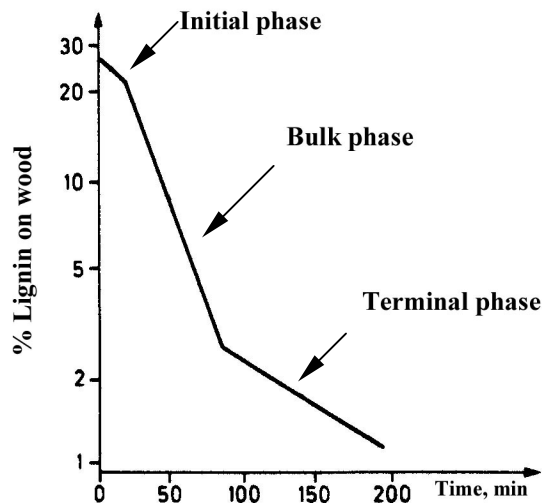
Figure I.1. Idealized lignin content (% on wood) versus reaction time for conventional softwood kraft pulping.

Bulk delignification is first order with respect to lignin concentration, almost linearly dependent on the hydroxide, but only slightly dependent on the hydrosulfide ion concentration. The activation energy of this phase of lignin degradation was found to be 150 kJ/mol, which is of the magnitude typically encountered in chemical reactions. The residual phase of delignification includes the final treatment at 170°C and leads to dissolution of roughly 10-15% of the lignin originally present in wood. This process is very slow, the rate being dependent on the temperature and hydroxide ion concentration, but almost independent of the hydrosulfide ion concentration. The activation energy was found to be about 120 kJ/mol. The selectivity for lignin in this phase is poor, as evidenced from an increased degradation of carbohydrates relative to the rate of delignification.[20] The cook should be terminated at this point to prevent significant loss of pulp strength, and the remaining residual lignin should be removed using alternative delignification techniques, such as oxygen delignification and/or chloride dioxide bleaching.[21]

Typically, residual lignin content for a conventional softwood kraft cook is in the range of 4-5% or 27-33 kappa number. Pulping to lower lignin content under these conditions causes severe degradation of the carbohydrate fraction, resulting in a pulp with poor papermaking qualities. The low rate of lignin dissolution could possibly be ascribed to

the fact that while reactions in the residual phase require high alkalinity, the concentration of alkali at this stage of pulping is considerably lower than during the preceding phases due to neutralization reactions with various degradation products, particularly those arising from carbohydrates. Acids formed during the degradation of carbohydrate degradation consume 60-70% of the charged alkali while 10% of the added alkali is used to neutralize uronic and acetic acids and 20-30% is consumed in solubilizing the degradation products of lignin. It is also possible that the degree of swelling decreases as a result of alkali shortage. A fiber wall in an unswelled state may resist diffusion. It has also been shown that dissolved lignin is precipitated inside the fibers when the alkalinity is lowered. It is therefore possible that a partially reversible precipitation of degraded but not dissolved lignins occurs when the alkalinity is lowered. Another reason for the poor selectivity of the residual phase of delignification is that the structure of the residual lignin that remains in the fiber at the end of the cook has a low reactivity toward the pulping chemicals, thereby making fragmentation and dissolution difficult.[22] Alternatively, several researchers have proposed that lignin dissolution is hindered by the attachment of the residual lignin to carbohydrates.[23, 24]

I. Review of Kraft Delignification Chemistry

The primary reaction of lignin during kraft pulping can be divided into two classes, degradation and condensation reactions. Degradation reactions lead to the liberation of lignin fragments and ultimately to their dissolution. These degradation reactions are therefore desirable to kraft pulping. Condensation reactions lead to the formation of alkali-stable linkages, thereby increasing the molecular size of lignin fragments and may result in their precipitation. Although having an opposite effect, these two types of reactions are intimately connected with each other by proceeding via common intermediates. There are other types of reactions occurring during kraft pulping. These reactions do not involve any net fragmentation of the lignin macromolecule, yet yield alkali-stable structures that make additional fragmentation difficult. Pulp carbohydrates also undergo alkali-catalyzed degradation reactions during the kraft pulping process that are detrimental to physical strength properties.[25]

Degradation or fragmentation reactions are the most important reactions occurring during kraft pulping because these reactions assist in the fragmentation and dissolution of the lignin polymer. The most prevalent degradation reactions occurring during kraft pulping include the cleavage of α-aryl ether and β-aryl ether bonds. However, the reactivity of such linkages is sensitive to the type of moiety (i.e., free or etherified phenolic group) present at the para position relative to the propane side chain. The α-aryl ether linkage is readily cleaved, the reaction involving an alkali-assisted rearrangement of the phenolate structure to the corresponding quinone methide structure with elimination of the α-aryloxy substituent. Figure I.2 illustrates this type of cleavage. Since no hydrosulfide ions are involved in the cleavage of α-aryl ether bonds, the rate of reaction is also independent of the concentration of these ions.[24, 26]
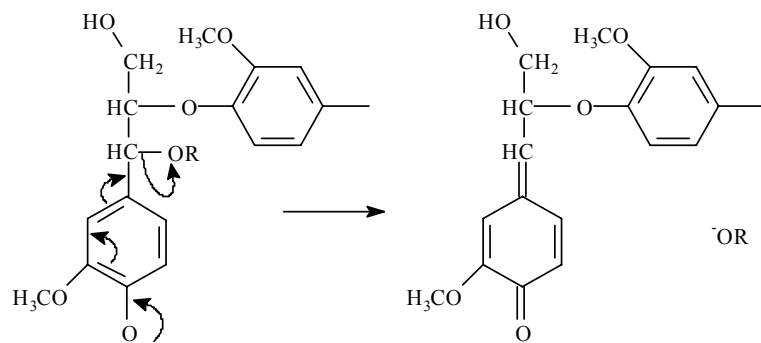
Figure I.2.   Alkaline cleavage of α-aryl ether bonds in phenolic phenylpropane units.

The cleavage of β-aryl ether bonds in phenolic units also proceeds rapidly, with the initial conversion into the quinone methide constituting the rate determining step in the overall reaction. Phenolic β-aryl ether structures can also undergo an alkali-assisted transformation into a quinone methide, provided a suitable leaving group exists at the α-position of the propane side chain. The quinone methide intermediate can then react in different ways to restore the aromaticity of the aromatic ring. The quinone methide could be converted into an alkali-stable enol ether structure through the elimination of the terminal hydroxymethyl group as formaldehyde. This reaction is more prominent in the absence of hydrosulfide ions, as is the case during soda pulping. However, enol ether structures have been detected in kraft residual lignin and this reaction pathway is therefore possible.

Under kraft pulping conditions, the hydrosulfide ion, which is a stronger nucleophile than hydroxide ion, readily reacts with the quinone methide intermediate to restore the aromaticity of the aromatic ring. The reversible addition of hydrosulfide ions results in the formation of a benzyl mercaptide structure. This mercaptide anion can then attack the β-carbon, through a neighboring group participation reaction thereby eliminating the β-aryloxy substitutent. Although the presence of hydrosulfide ions is believed to influence the reaction pathway resulting in the fragmentation of the aryl ether linkage, enol structures have been detected in kraft residual lignin, suggesting that both reaction pathways in Figure I.3 can occur during kraft pulping. The initial phase of delignification is characterized by a low activation energy, hence lignin fragmentation reactions that occur during this phase must occur at the same or higher rate than diffusion. This requirement is met by the cleavage of α- and β-aryl ether linkages in phenolic units. Thus, the degradation of lignin during the initial phase, involving only phenolic units, may continue until it reaches units which are not of the α- or β–aryl ether type (peeling of lignin).[21]
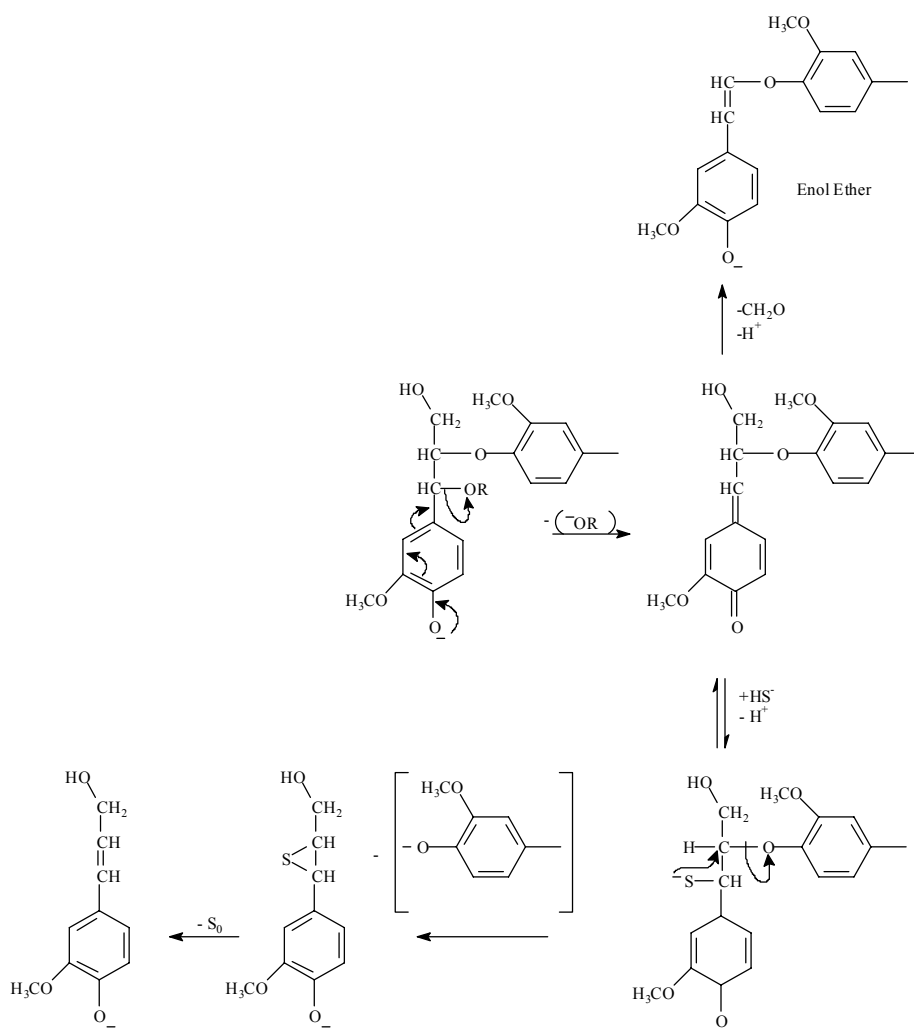
Figure I.3. Sulfidolytic cleavage of β-aryl ether bonds in phenolic phenylpropane units and conversion into enol-ether units.

When phenolic units of the α- and β-aryl ether types have been degraded in a kraft pulp further lignin degradation requires more drastic conditions such as those prevailing during the bulk phase of delignification of kraft pulping. Cleavage of α- and β-O-aryl ether linkages in phenolic units, proceeding much faster, cannot be rate-determining during this phase. Instead, on account of similarities between the kinetic data, the cleavage of β-O-aryl ether bonds in non-phenolic units has been considered as the rate determining reaction in the overall bulk delignification. The cleavage of β-aryl ether linkages in non-phenolic structures is a relatively slow reaction that is dependent on the phenylpropane units having a hydroxyl group on the α- and γ-carbon. This group can dissociate under extreme alkaline conditions, forming an alkoxide anion. A nucleophilic attack on the β-carbon, through a neighboring group participation reaction, results in an oxirane intermediate with concomitant elimination of the β-aryloxy substitutent. Subsequent attack by the nucleophiles found in the cooking liquor (hydroxide and hydrosulfide ions) breaks the epoxide ring, producing diols or thioglycol-type structures as shown in Figure 1.4.
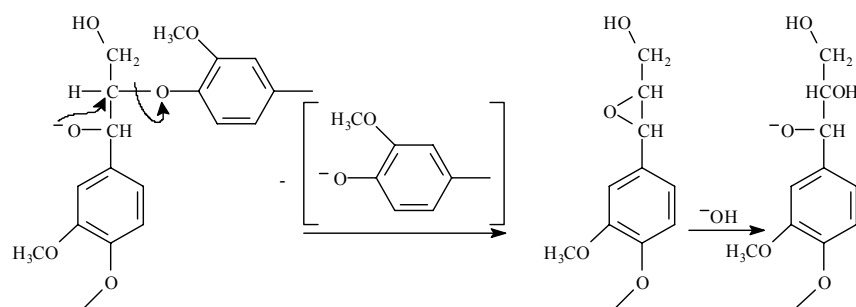
Figure I.4. Alkaline cleavage of β-aryl ether bonds in non-phenolic phenylpropane units.

Cleavage of β-aryl ether linkages in non-phenolic units also liberates new phenolic structures that may constitute the starting point for the two types of cleavage reactions operating during the initial phase, i.e., cleavage of α- and β-aryl ether bonds in phenolic units. As a result of these reactions, lignin degradation during the bulk phase, initiated by the rate determining cleavage of β-aryl ether bonds in non-phenolic units, is extended to the point where dissolution takes place. Thus the subsequent fast reactions have no influence on the rate, but a great influence on the extent of lignin degradation. In this way, they contribute extensively to the rate of lignin dissolution during the bulk phase.

Unlike the fragmentation reactions of ether linkages, the cleavage of carbon-carbon bonds during kraft pulping account for only a small amount of the total lignin fragmentation. This cleavage occurs in side chains and between side chains and aromatic nuclei, often resulting in the formation of new carbonyl linkages.

Lignin degradation and fragmentation reactions are believed to be counter-balanced by condensation reactions during kraft pulping. Primary condensation reactions occur when quinone methide intermediates are formed by the elimination of an α-substitutent while secondary condensation reactions occur with quinone methide structures formed after an initial ether cleavage. Condensation reactions may be viewed as conjugate additions in which quinone methides, extended quinone methides or side chain enone structures function as acceptors, and carbanions from phenolic or enolic units serve as adding nucleophiles.

In summary, kraft pulping has a dramatic effect on the nature of residual lignin in kraft pulps and is dependent upon the cooking technologies employed along with cooking parameters. In brief, as pulping is extended kraft residual lignin has less β-O-aryl ether linkages, more condensed phenolics and etherified units, enhanced amounts of p-hydroxyl phenolics and elimination of δ-hydroxyl groups. In prior research activities Ragauskas et al.[27] Lai et al.[28] and others[29] have demonstrated that these changes in residual lignin impact pulp bleachability with several ECF and TCF bleaching technologies. Several of these changes in lignin structure were readily anticipated to

influence the reactivity of kraft pulps towards to oxygen delignification especially since the primary site of lignin reactivity in an oxygen-stage are phenolic hydroxyl groups.

## I. Review of Fundamentals of Oxygen Delignification

Oxygen bleaching is typically used as an extended delignification method to remove lignin before using more expensive bleaching chemicals. Delignification up to 50% can be achieved using an oxygen bleaching stage. Oxygen essentially acts as a free radical and attacks electron-rich sites on the substrate. The mechanism of oxygen bleaching has been studied using changes in model compounds as well as structural changes in both residual and dissolved lignins.

Free phenolic hydroxyl groups are a predominant site for attack once the hydroxyl group has been ionized due to the alkaline conditions. An electron is then removed from the phenolic oxygen using a suitable acceptor such as molecular oxygen or other radicals present in the system. The radical can exist at either the phenolic oxygen, any one of several aromatic carbons, or at the β-carbon as shown in Figure I.5.
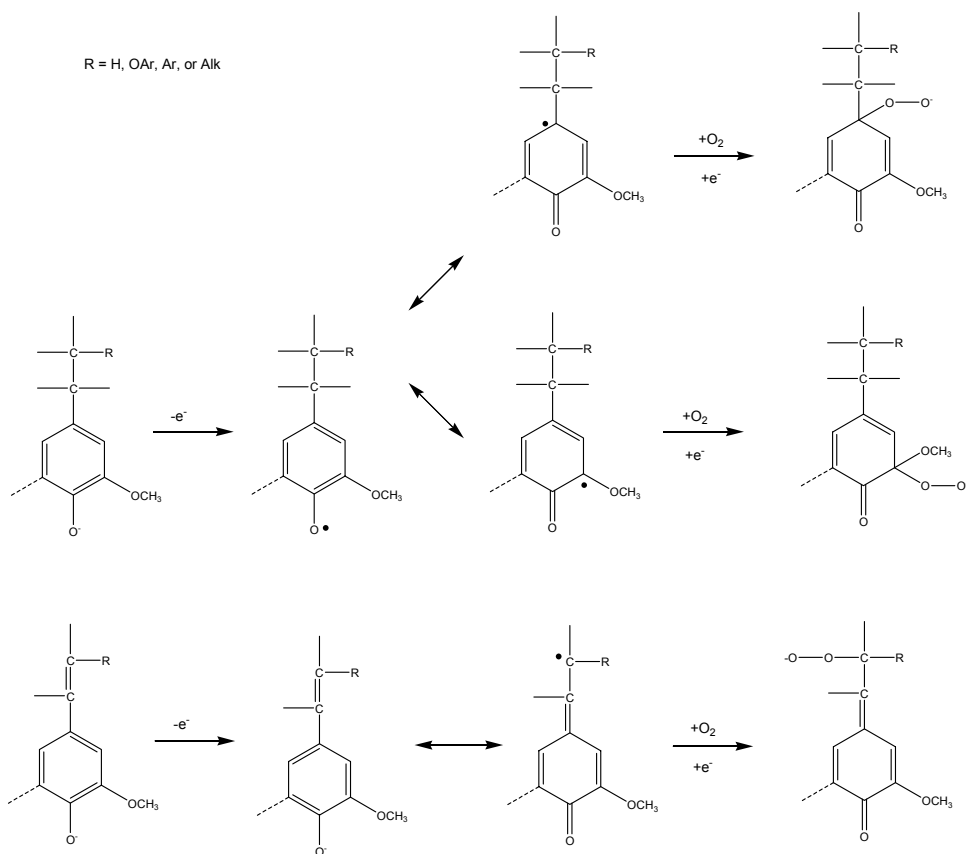
Figure I.5. Initial reactions in oxygen delignification.

The intermediates, hydroperoxides, can undergo several reactions that may result in the formation of oxiranes, muconic acid, and carbonyl structures. The formation of the oxiranes and muconic acids will introduce hydrophilic groups into the lignin structure, thus increasing its solubility. The introduction of carbonyl structures indicates the breaking of interunit linkages which also increases the solubility of the lignin. These reactions are shown in Figure I.6.
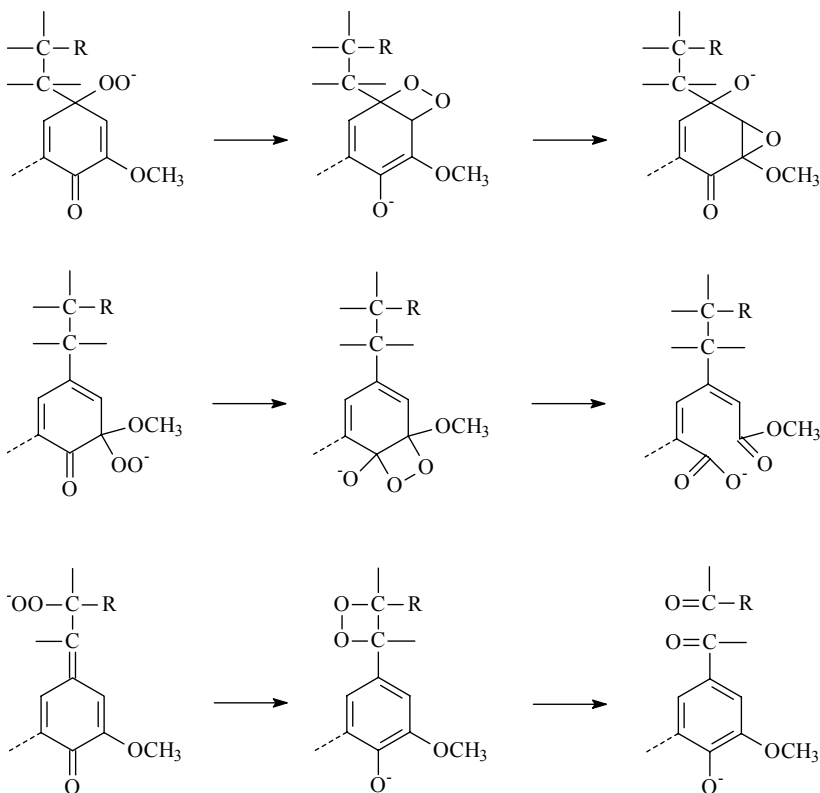
**Figure I.6.** Reactions of hydroperoxide intermediates.

The formation of quinone structures from hydroperoxide intermediates may also occur. The quinone structures may undergo a nucleophilic attack from a hydrogen peroxide anion which results in the opening of the ring and formation of muconic acids. Condensation products may also be formed during oxygen bleaching. The phenoxy radicals that are formed in the initial reactions may undergo coupling reactions resulting in carbon-carbon bonds between lignin units. These condensation products will increase the molecular weight of the lignin and decrease its solubility as well as making the lignin unreactive to the attack of oxygen.

I. Review of Residual Lignin Distribution after Oxygen Delignification

An oxygen-delignification stage will typically remove 35-50% of the remaining lignin in the pulp before significant cellulose degradation occurs. The lignin removed from the pulp during oxygen delignification is primarily taken from the interior of the fiber as demonstrated by Laine et al.[31] Oxygen removes only 15% of the surface lignin while decreasing the total lignin content of the pulp by approximately 50%. In a study by
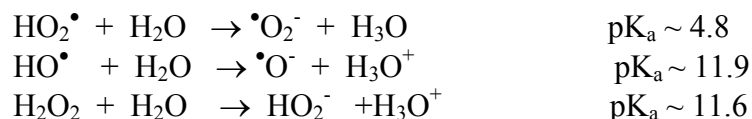
Wang et al., oxygen treatment resulted in a more efficient delignification of the S_2 cell wall layer.[32] Pereria has also studied the effect of oxygen bleaching on the surface lignin content of the fiber using atomic force microscopy.[33] The regular lignin patches on the surface of the unbleached fiber are decreased in size after oxygen treatment.

In an O-stage the oxidant is oxygen and associated species. It is well known that as oxygen reacts with the substrate, it can be reduced to water by one-electron transfer in four successive stages giving rise to intermediate products, namely, hydroperoxy radical ($HO_2^{\bullet}$), hydrogen peroxide (H_2O_2), and hydroxyl radical ($HO^{\bullet}$) as well as their counterparts as shown in Figure I.7.
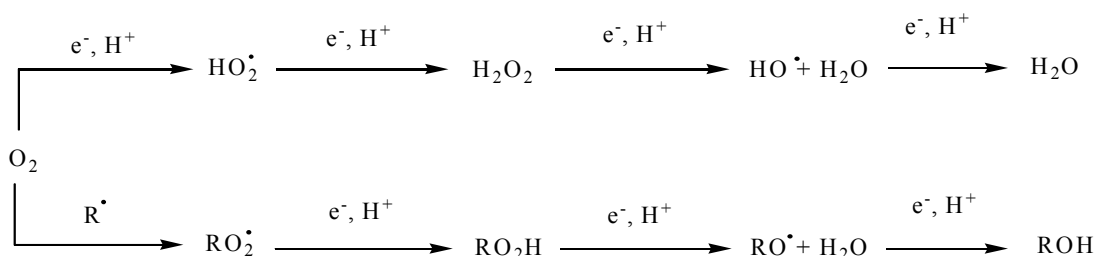

Figure I.7. Reduction of oxygen by one-electron transfer mechanism.

When the pH of the medium is sufficiently high, ionization will take place as follows:

$$HO_2^{\bullet} + H_2O \rightarrow {}^{\bullet}O_2^- + H_3O \qquad pK_a \sim 4.8$$
$$HO^{\bullet} + H_2O \rightarrow {}^{\bullet}O^- + H_3O^+ \qquad pK_a \sim 11.9$$
$$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+ \qquad pK_a \sim 11.6$$

Since bleaching with oxygen is normally performed at a rather high pH, the reactive species generated from oxygen include hydrogen peroxide anion (HO^-) and dissociated oxide and superoxide hydroxyl radical ($^{\bullet}O^-$, $^{\bullet}O_2^-$), as well as undissociated and highly reactive hydroxyl radical ($HO^{\bullet}$). Usually, superperoxide radical ($^{\bullet}O_2^{-}$) may diffuse some distance but hydroxyl radical ($HO^{\bullet}$) reacts where it is created.

The complex oxidation processes that occur in the oxygen delignification include similar radical chain reaction involving a variety of organic species derived from both lignin and carbohydrates. In oxygen bleaching, the substrate is activated by providing alkaline conditions to ionize free phenolic hydroxyl groups in the residual lignin. The resulting anionic sites are electron-rich and therefore vulnerable to attack by oxygen. An electron is abstracted, forming superoxide anion and a phenoxy radical which react further with oxygen (see Figure I.8).
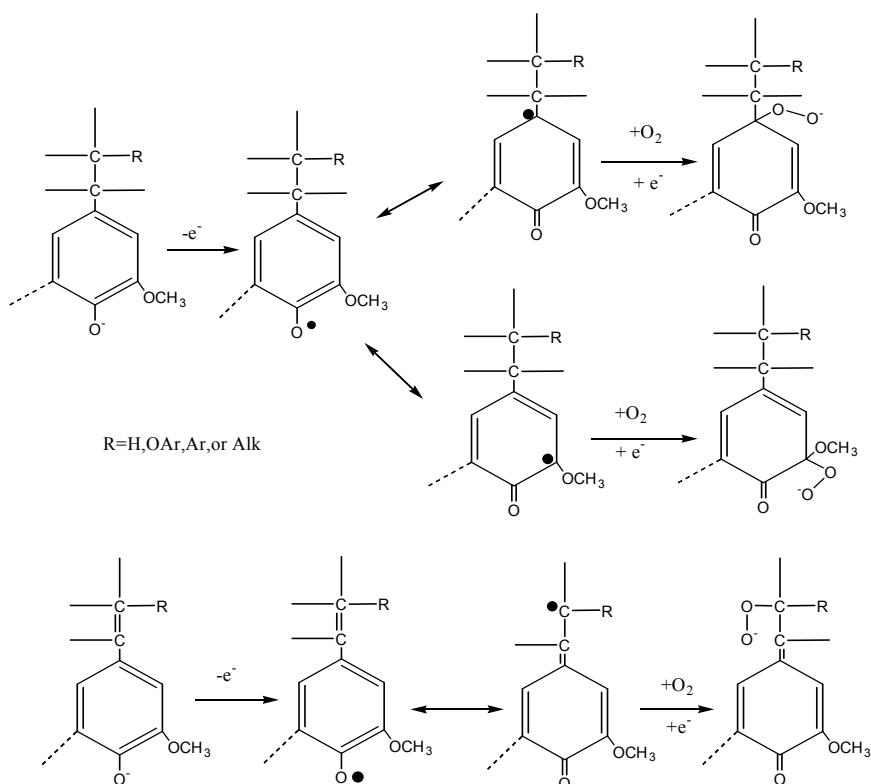
Figure I.8. Initial reactions leading to oxygen delignification.

Kraft pulps always contain trace amounts of transition metals (mainly Fe, Co, Cu, and Mn in different valence states). These metals act as effective catalysts decomposing peroxides to hydroxyl radicals (see eq. 1 and 2) that are believed to be the source of much of the damage to cellulose that occurs during oxygen delignification.

$$H_2O_2 + M^{n+} \rightarrow HO^{\bullet} + HO^- + M^{(n+1)+} \tag{1}$$
$$HO_2^- + M^{n+} \rightarrow {}^{\bullet}O^- + HO^- + M^{(n+1)+} \tag{2}$$
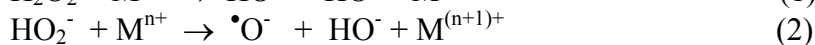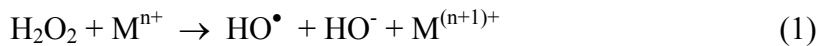
In a neutral aqueous solution, the hydroxyl radical is an electrophilic reagent with very strong oxidizing properties (standard redox potential $E^0 \sim 2.3$ V), but after ionization at higher pH values, it decreases its electrophilic character and the redox potential of the resulting anion (${}^{\bullet}O^-$) is substantially lower ($E^0 \sim 1.4$ V). The hydroperoxide radical ($HO_2^{\bullet}$) is ionized even in a weakly acidic medium due to its lower acidity constant ($pK_a \sim$ 4.8). The ionized superoxide (${}^{\bullet}O_2^-$) is a weak oxidant ($E^0 \sim 0.41$ V), thus having more selective properties. The hydrogen peroxide anion (HO_2^-) is a rather weak oxidant ($E^0 \sim$ 0.87 V).

I. Review of Effect of Mg^{2+} on Oxygen Delignification

Selectivity of oxygen delignification can be defined as the ratio of attacked on lignin to attack on carbohydrate, expressed as $\Delta kappa_{(intitial-final)}/\Delta viscosity_{(initial-final)}$. It is affected by the choice of process conditions and by the presence of pulp contaminants. Of the factors governing selectivity in oxygen bleaching, one of the most important is the transition metal content in the pulp, because these metals catalyze the generation of harmful radical species. Most pulps contain appreciable quantities of iron, copper, and manganese, all of which have this effect. One approach for dealing with transition metals is to remove them by acid washing before the oxygen stage; another is to add compounds to the pulp that inhibit carbohydrate degradation, which are called carbohydrate protectors.

To-date the magnesium compounds, such as MgSO$_4$, are the best and most widely used to improve the selectivity of an O-stage. It is normally applied at levels as low as 0.05-0.1 % Mg^{2+} on oven dry pulp. It is believe to function by precipitating as magnesium hydroxide, which adsorbs the metal ions, making them unavailable for catalysis of peroxide decomposition[34] or by forming complexes with them.[35] Researchers in the past several years have speculated that Mg^{2+} co-precipitates with Mn^{2+} ion into a "soluble" aggregate that essentially neutralizes the redox activity of Mn^{2+}. They determined that the minimum Mg/Mn molar ratio required to offset the redox activity of Mn^{2+} is approximately 30 (mol/mol). The study by Lucia and Smereck[37] demonstrated that the Mg addition acts to mitigate the activity of the Mn ion at all temperatures (80 and 100°C) and time (60 and 80 min), by reducing the fluctuations in the viscosity level. High Mg/Mn molar ratio (33:1) demonstrates an important increase in viscosity selectivity than in low Mg/Mn molar ratio (22:1). The highest selectivity at both temperatures for both pulps (with kappa number of 39.8 and 25.3) was obtained with the high Mg/Mn ratio at short time. However, the higher protective metal ratio cannot compensate for the damaging effect of higher temperature, which accelerates cellulose degradation. Figure I.9 illustrates the effectiveness of magnesium in preserving pulp viscosity and is typical of selectivities obtained in the bleaching of softwood kraft pulp.[38]
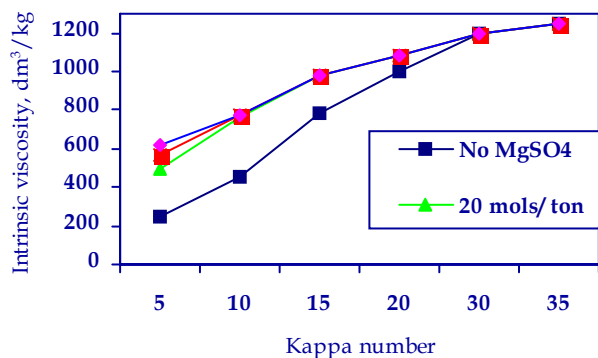
Figure I.9. The relationship between viscosity and kappa number for oxygen delignified softwood kraft pulp.

I. Review of Oxygen Delignification and Carbohydrates Degradation

At fixed alkali concentration and temperature, the typical delignification process indicated by kappa number reduction with time was characterized by two distinct stages: an initial rapid phase and a slower phase as shown in Figure 1.10. The two-delignification stages are directly paralleled by two corresponding cellulose depolymerization as summarized in Figure I.11.
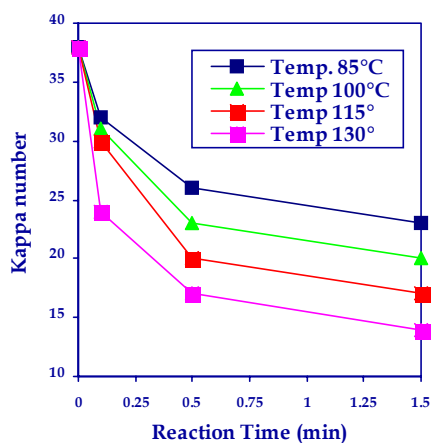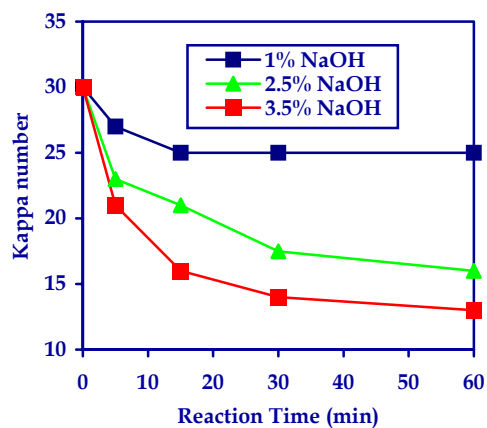
(a)   (b)

Figure I.10. O_2 delignification rate of softwood kraft pulp under different temperatures (a) and alkaline (b) conditions.

Figure I.11. The rate of viscosity reduction in O_2 delignification of softwood kraft pulp under different alkaline conditions.

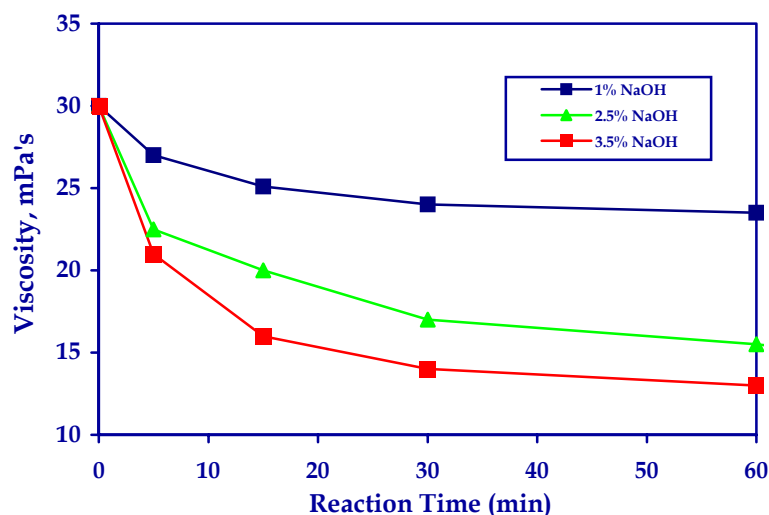This behavior is interpreted as being caused by the presence of two types of residual lignin that differ in case of removal by oxygen. The first type is removed within about 5-15 minutes, which should be attributed to those very reactive structures toward oxygen species in residual lignin such as catechols, stilbenes, and enol ethers. Additional phenolic hydroxyl and unsaturated groups in the side chain are both structural features that enhance reactivity. A methoxyl constituent in the aromatic ring also increases the reaction rate Lai, et al. reported that the initial rapid phase for oxygen delignification of Norway spruce kraft pulp entered at a kappa number of 20, which is largely attributed to the degradation of condensed units originated in the wood lignin, probably associated with the phenylcoumaran-type structures such as β-5 linked phenylcoumaran structures.[28] Some structural units that have free phenolic hydroxyl groups are reactive but exhibit slow rate. An inter-unit linkage at 5 position of the aromatic ring decreases the rate. In addition, diphenylmethane type condensed units formed in kraft pulping were fairly resistant to degradation and may also be a key contributing factor to the slow phase of the O_2 delignification process.

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Program Deliverables: Extended Oxygen Delignification

Chapter II. Low Capital O-Delignification

As discussed by several industry leaders, the production of wood pulp is not providing sufficient return on equity for the amounts of capital required to produce bleached kraft pulp.[1,2] This poses a new challenge for researchers in the field of kraft pulping and bleaching operations. Certainly, several research groups have begun to address this issue, and publications by Stapley et al.,[3] Null and Cenatempo,[4] Kimbrel,[5] Tait,[6] McDonough et al.,[7] Chakar et al.,[8] and Histed[9] are reflective of this effort.

Although the capital costs of an oxygen stage are substantial, it is generally believed that the overall performance of an O-stage can be significantly improved, thereby improving the overall return on capital. Extended oxygen delignification studies by Magnotta et al.,[10] Bokstrom and Norden,[11] and Steffes et al.[12] indicated that distinct yield benefits can be accomplished by halting the cook at a high kappa number before the selectively of the kraft cook decreases in the terminal phase. Extended oxygen delignification of high kappa pulps followed by ECF bleaching has been shown to provide 3-4% yield benefits over conventional bleaching technologies. Minja et al.[13] and Parthasarathy[14] have proposed that coupling this approach with PS/AQ kraft cooking and pulping additives can provide additional 2-3% yield improvements. These observed yield benefits are then further amplified by reducing the organic load on the recovery furnace, which has potential productivity benefits for recovery boiler-limited mills.[15]

Typically, oxygen delignification is limited to 50% of the brownstock kappa number. However a recent survey of pulp mill practices suggested that many mills do not achieve even this level of performance.[16] Extending practical delignification past 50% typically requires the use of double-stage oxygen delignification technologies. These systems have been shown to result in 55-67% delignification for commercial operations.[17-20] Unfortunately, these operational benefits are accompanied by additional capital costs. An alternative approach to utilizing oxygen delignification chemistry in pulp bleaching is the application of a mini-O system. This system typically removes lesser amounts of lignin but requires less capital investment and is readily retrofitted to existing pulp bleaching operations. Histed[21] 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 a SW kraft pulp. McKenzie et al.[22] reported that the commercial use of a mini-oxygen delignification system prior to a conventional O stage provided an additional 25% delignification of a SW kraft pulp. Typically, a mini-O stage employs an upflow tube with retention of approximately 30 minutes, oxygen pressure of 80–90 psig, 1% NaOH, held at 70–80°C. A single mini-O stage has been reported to remove 25% of the lignin in a kraft brownstock and the fundamental bleaching and process chemistry associated with this technology.[23] Treatment of a 26.6 kappa number SW kraft pulp with (E+O) was found to remove 13-25% of the lignin in the pulp depending on the charge of caustic employed (i.e., 1.5–3.5%). The delignification effects of the (E+O) treatment were shown to be dramatically improved if

the caustic charge was split into two and the pulp was oxidized with a low charge of chlorine dioxide after the initial (E+O) stage (see Figure II.1).
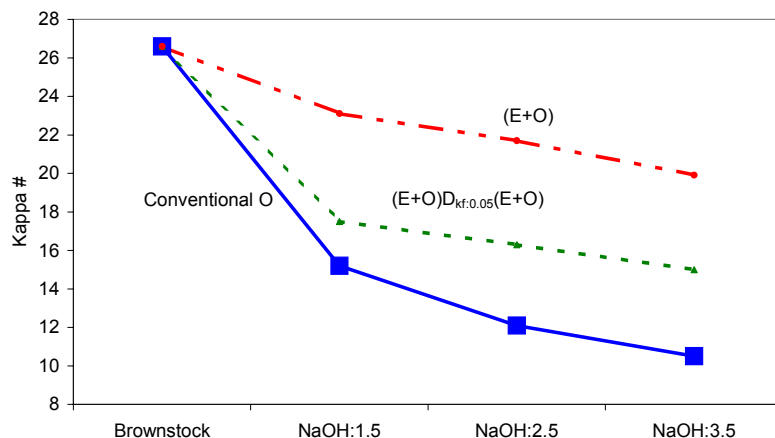
Figure II.1. Delignification SW kraft pulp employing O, (E+O), and $(E+O)D_{kf:0.05}(E+O)$ employing total NaOH charges of 1.5, 2.5, and 3.5%.[23]

The delignification effects observed in this process were shown to be due to the partial oxidation of phenolic lignin groups by the (E+O) and D treatments. In addition, the benefits of the mini-O system could be attributed, in part, to the extraction of leachable lignin present in kraft brownstock pulp.[24,25] This study further examines the benefits of a mini-O system and the effects of pulp washing. These results are then compared against a conventional oxygen stage.

Chapter II. Experimental

An industrial SW kraft pulp with a kappa number of 26.2 and viscosity value of 33.2 cP was employed for experiments in this study. Prior to any delignification studies, the pulp was extensively washed until the wash water was pH neutral and colorless.

Chlorine dioxide bleaching studies were accomplished in a quantum mixer following the conditions described in Table 1. The O and mini-O reactions were performed in a pressure vessel following the conditions summarized in Table 1.

Delignified pulps were analyzed for kappa number following TAPPI Standard Method T236.[26] Typical experimental standard deviations for this procedure were determined to be 2.0%. Pulp viscosity values were determined in accordance with TAPPI Standard T-230 om-89,[26] and standard deviations were 0.4.

## Chapter II. Results and Discussion

Oxygen pulp bleaching effects were performed employing a commercial SW kraft pulp with kappa number of 26.2. Oxygen bleachability of this pulp was examined employing conventional and mini-O bleaching sequences; the experimental conditions employed are summarized in Table II.1.

Table II.1. Oxygen and mini-oxygen bleaching conditions.

Oxygen Stage(s)	Conditions
O	10% csc, 90°C, 60 min., 2.5% NaOH
D	0.20 kf ClO$_2$, 10% csc, 70°C for 30 min.
D$_{kf:0.05}$	0.05 kf ClO$_2$, 10% csc, 70°C for 30 min.
(E+O)*	10% csc, 80°C, 40 min., 2.5% NaOH
(E+O)	10% csc, 80°C, 20 min., 1.25% NaOH

Note: all O and (E+O) treatments employed 0.10% MgSO$_4$ and the O$_2$ pressure was held constant at 90 psig.

The delignification results achieved employing O, (EO)*, (EO)(EO), D$_{kf:0.20}$(E+O), D$_{kf:0.05}$(E+O)(E+O), and (E+O)D$_{kf:0.05}$(E+O) on a kappa 26.2 SW kraft pulp are summarized in Figure II.2.
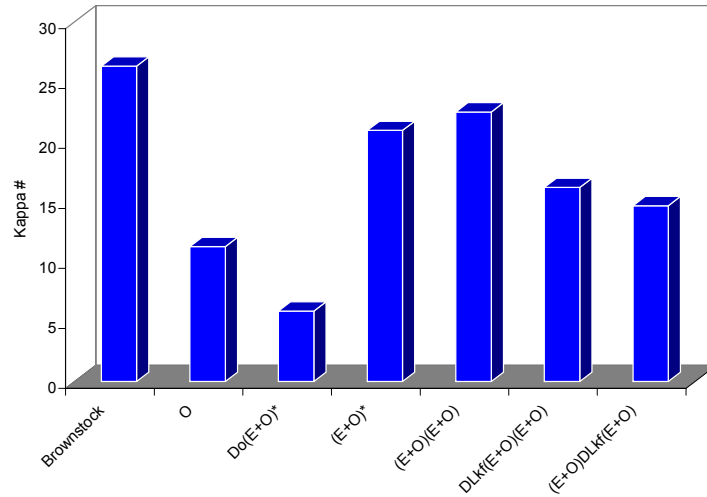

Figure II.2. Delignification of SW kraft pulp (kappa 26.3) employing O, (E+O)*, D(E+O)*, (E+O)(E+O), D$_{kf:0.05}$(E+O)(E+O), and (E+O)D$_{kf:0.05}$(E+O) with washing between each bleaching stage.

The results of these initial studies yield several interesting conclusions including that a limited amount of lignin can be abstracted from the pulp employing either (E+O) or (E+O)(E+O) (i.e., 20 and 14%, respectfully). Since both of these treatments employed equal amounts of caustic, splitting the charge of NaOH between two (E+O) stages is not beneficial with respect to delignification. Of greater practical interest, is the 38% delignification of D$_{kf:0.05}$(E+O)(E+O) and 44% delignification of (E+O)D$_{kf:0.05}$(E+O). Although these treatments are not as efficient as the conventional O-stage (57% delignification) or an D$_{0.20\ kf}$(E+O) treatment (78% delignification), the application of a low charge of chlorine dioxide prior to a mini-O treatment sequence can significantly improve the performance of a mini-O system. Presumably, the improved delignification of (E+O)D$_{kf:0.05}$(E+O) over D$_{kf:0.05}$(E+O)(E+O) can be attributed to the initial (E+O) stage removing easily oxidized lignin prior to the low kappa factor charge of chlorine dioxide.

Hence, the $(E+O)D_{kf:0.05}(E+O)$ sequence more efficiently utilizes the low charge of chlorine dioxide.

The viscosity values for the pulps described in Figure II.2 are summarized in Figure II.3. These results demonstrate that the milder bleaching conditions of the $D_{kf:0.05}$ mini-O bleaching sequences allowed for improved pulp viscosities.
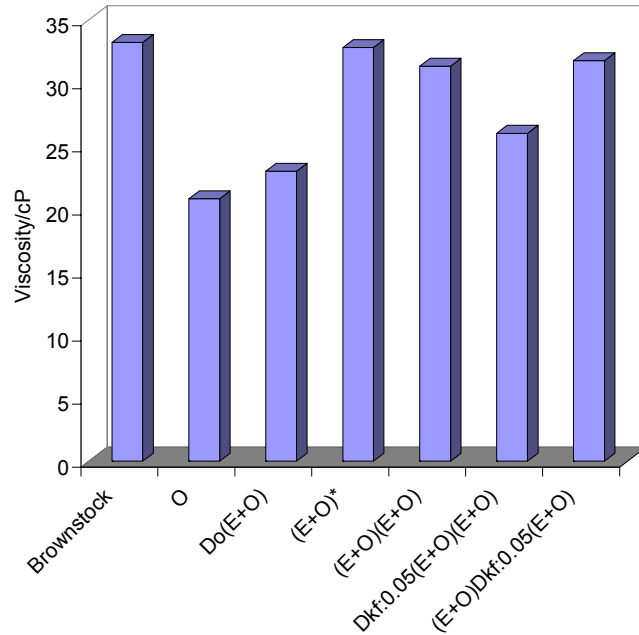
Figure II.3.   Pulp viscosity (cP) values of SW kraft pulp (kappa 26.3) treated with O, (EO)*, D(EO)*, (E+O)(E+O), $D_{kf:0.05}(E+O)(E+O)$ and $(E+O)D_{kf0.05}(E+O)$ and washed between stages.

Despite these promising results, the use of interstage washing employed in the initial studies would limit any practical applications of these sequences. To examine this issue, we repeated the mini-O sequences without any washing between the stages, and these results are summarized in Figure II.4.
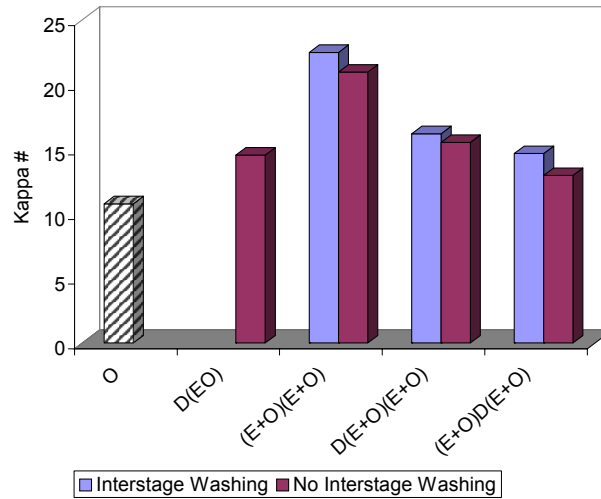
Figure II.4. Effects of washing on delignification properties of $(E+O)(E+O)$, $(E+O)D_{kf:0.05}(E+O)$ and $D_{kf:0.05}(E+O)(E+O)$.
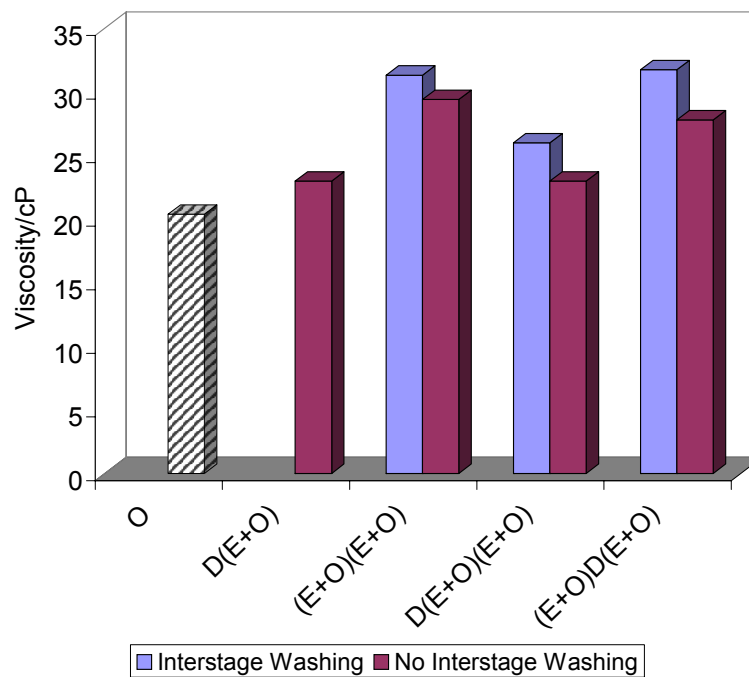
Figure II.5. Effects of washing on pulp viscosity properties of $(E+O)(E+O)$, $(E+O)D_{kf:0.05}(E+O)$ and $D_{kf:0.05}(E+O)(E+O)$.

The results in Figures II.4 and II.5 indicate that there are no significant detrimental impacts on either $(E+O)D_{kf:0.05}(E+O)$ or $D_{kf:0.05}(E+O)(E+O)$ caused by not employing interstage washing.

Chapter II. Conclusions

The mini-O treatments described in this section serve to highlight the potential practical applications of a mini-O system to pulp bleaching operations. The negligible effects of not washing the pulp between mini-O treatments suggest that inter-stage washing may not be required. Further, it may be possible to extend the benefits of a mini-O system by reinforcing it with low charges of hydrogen peroxide.

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Chapter III. Improved O-Delignification via Mini-O

Although ECF bleaching technologies have been shown to address environmental concerns and produce pulps with desirable quality properties, the conversion to these bleaching operations has been accompanied by increased costs.[1] Clearly, the challenge that now needs to be addressed is how ECF bleaching technologies can be utilized to minimize capital and operating costs. Several research groups have begun to address this issue and publications by Tait,[2] Stapley et al.,[3] Null and Cenatempo,[4] Kimbrell,[5] and Chakar et al.[6] are indicative of this endeavor.

A mini, (E+O), or poor man's oxygen system provides an alternative approach to utilizing oxygen delignification technologies. This system usually removes less lignin but requires less capital investment than a typical oxygen delignification system and is easily retrofitted to existing pulp bleaching operations.[7] Equipment and conditions required for a mini oxygen stage are similar to those currently applied in oxygen and hydrogen peroxide-reinforced extraction stages in the bleach plant. Typically, a mini oxygen delignification stage uses an upflow tube with a retention of about 30 minutes, oxygen pressure of 80-90 psig, 1% NaOH, held at 70-80°C.[1] McKenzie reported that the commercial use of a mini oxygen system has produced low AOX pulps with no loss of production due to recovery or recausticizing bottlenecks. In addition, the mini oxygen stage provided approximately 25% delignification prior to a conventional oxygen stage.[8]

Recent research efforts have focused on extending the capabilities of the poor man's oxygen delignification technologies.[9] Histed has proposed using an enhanced poor man's oxygen stage to achieve higher levels of delignification. The enhanced poor man's oxygen, which is 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.[10] Chakar et al. demonstrated that (E+O) treatment of a 26.6 kappa number softwood resulted in 13-25% delignification, depending on the caustic charge. These researchers also showed that the delignification effects of the (E+O) treatment were improved dramatically if the caustic was divided in half and the pulp was treated with a low charge of chlorine dioxide after an initial mini oxygen stage.[6] Dyer et al. further examined the benefits of an enhanced poor man's oxygen stage. They demonstrated that a $(E+O)D_{0.05}(E+O)$ had 6% more delignification than a $D_{0.05}(E+O)(E+O)$. The authors attributed this enhanced delignification to the initial (E+O) stage removing easily oxidized lignin prior to the low kappa factor charge of chlorine dioxide.[1]

In an effort to further extend the performance of a poor man's oxygen stage, it would be useful to investigate the impact of black liquor carryover on this ECF bleaching technology. Dissolved material in an oxygen stage, unlike that from chlorination and following extraction stages, is uncontaminated by chloride ions. It can therefore be routed back to the recovery furnace, where it becomes a source of energy instead of a pollutant.[11,12]

Enz and Emmerling reported that a raw black liquor solids addition of 65 kg/o.d. ton had no impact on the delignification or pulp physical properties of a commercial oxygen

delignification system. In fact, this stability allowed the mill to use a low average dilution factor to the brownstock washing system.[13] Several researchers have investigated the impact of inefficient washing systems on laboratory oxygen delignification systems. There is some evidence that small amounts of black liquor carryover might benefit an oxygen delignification system. Miller,[14] Parthasarathy,[15] and Parsad et al.[16] reported increases in delignification at the addition rates used in their studies. The apparent reason for this increase in delignification is due to residual alkali left in the carryover. However, several other research groups have found that black liquor carryover impacts both alkali and oxygen consumption due to the competing reactions between pulp lignin and dissolved material in the liquor.[17,18] This lowers the delignification rate and may even enhance the selectivity of the oxygen delignification system.[19-22] Although there has been a significant contribution to the effects of black liquor carryover on an oxygen delignification system, the effects on a mini oxygen system and other ECF bleaching technologies are not yet clear. This study examined the performance of a mini-O stage incorporated with chlorine dioxide, hydrogen peroxide, and chelating stages in an attempt to elucidate the impact of black liquor carryover on the overall performance of these ECF bleaching technologies.

Chapter III. Experimental

Materials   A series of three commercial SW kraft pulps were employed for the mini oxygen delignification studies in this paper. Two preoxygen stage pulps had kappa numbers of 26.3 and 24.2, respectively, while a postoxygen pulp had a kappa number of 8.9. The preoxygen pulps had respective viscosity values of 27.4 and 26.5 cP while the postoxygen pulp had a viscosity value of 21.0 cP. Prior to the mini oxygen delignification studies, the pulps were extensively washed until the wash water was pH neutral and colorless. All chemicals employed for these studies, with the exception of chlorine dioxide, were purchased commercially and used as received.

Metals Analysis of Pre- and Post-O_2 Pulps   Nonprocess elements of the kappa 24.2 and 8.9 SW kraft pulp were determined using standard ICP methods.[23] Table III.1 summarizes the results of the ICP analysis.

Table III.1. Metals analysis (ppm) of pre- and post-O_2 pulps.

Metal	24.2 Kappa Pre-O_2 SW Kraft Pulp	8.9 Kappa Post-O_2 SW Kraft Pulp
Fe	12	10
Co	<1	<1
Mn	36	32
Mg	510	482
Ni	2	<1
Cu	<1	13
Cr	<1	<1
Na	1310	280
Ca	1315	1555
K	86	94

Mini Oxygen Delignification. A 1000-mL capacity Parr reactor equipped with a stirrer, a pressure gauge, a heating mantle, and connected to a Parr 4842 temperature controller was charged with 20.0 grams of never-dried fibers (solids basis). The pulp consistency was adjusted to 10% by adding distilled water. Table III.2 summarizes the delignification conditions.

Table III.2. Mini-oxygen bleaching conditions.

Stage	O_2 Pressure/ Psi	NaOH/%	H_2O_2/%	$MgSO_4$/%	Temp./°C	Time/Min.
(E+O)	90	1.25	-	0.1	80.0	20.0
(E+P+O)	90	1.25	0.5	0.1	80.0	20.0
O	90	2.50	-	0.1	105.0	60.0

Chlorine Dioxide Stages. The chlorine dioxide (D) stages were performed on 20.0 grams of never-dried fibers (solid basis) at 10% consistency in sealed plastic bags immersed in a constant temperature water bath. Table III.3 summarizes the experimental conditions for these stages.

Table III.3. Chlorine dioxide stage conditions.

Stage	Kappa Factor	Exiting pH	Temp./°C	Time/min.
D	0.05	2.2	70.0	30.0
D	0.20	2.2	70.0	30.0

Pulp Characterization. Delignified pulps were analyzed for kappa number following TAPPI Method T 236 cm-85.[24] Typical experimental standard deviations for the preoxygen pulps were determined to be 0.09 and 0.08 for the post oxygen pulps. Pulp viscosity values were determined in accordance with TAPPI Method T 230 om-89 and standard deviations for the preoxygen pulps were 0.6 and 0.2 for the pre- and post oxygen pulps, respectively.[24] Pulp brightness measurements were reported as ISO brightness and

were performed in accordance with TAPPI Method T 525 om-92.[24] Typical brightness standard deviations for the pre-oxygen pulps were determined to be 0.1 and 0.08 for the postoxygen pulps. The handsheets for these measurements were made using TAPPI Method T 218 sp-97.[24] Nonprocess elements of the pre- and post oxygen pulps were determined using standard ICP methods.[23]


Chapter III. Results and Discussion

Mini O_2 and Black Liquor Carryover.   Previous studies reported by Chakar et al. and others[1,810,25] have shown that the delignification effects of a mini oxygen treatment are improved if the caustic charge is split into two and the pulp is oxidized with a low charge of chlorine dioxide. Furthermore, Dyer et al.[1] have shown that there are no significant detrimental impacts on a $(E+O)D_{0.05}(E+O)$ sequence when not employing interstage washing. These studies are beneficial to understanding the advantages of an enhanced poor man's oxygen stage although the conditions employed for these studies may not mimic an actual bleach plant setting. As a result, the impact of black liquor carryover on mini oxygen delignification as well as other ECF bleaching technologies is not fully understood.

This study explores the impact of black liquor carryover on mini oxygen delignification as part of a sequence using chlorine dioxide. The experimental conditions were selected from previous literature reports.[1,26] The consistency of all the stages was maintained at 10% while a constant charge of magnesium sulfate in the mini oxygen stages was employed to minimize the number of experimental variables. The mini oxygen delignification studies were maintained at an oxygen pressure of 90 psi and were stirred at a constant rate throughout the experiment. Black liquor was added to the pulp at two different charges, 2 and 10 kg solids per o.d. ton of pulp. There was no interstage washing employed in any of the studies employing black liquor carryover. These results were then compared to control studies that did not employ any black liquor or bleach plant effluent.

The delignification response for the 26.3 kappa SW kraft pulp under varying mini oxygen delignification conditions is summarized in Figure III.1. It is interesting to observe that the black liquor carryover seemed to enhance delignification under most cases except where the chemical charge was high, i.e., $D_{0.20}(E+O)(E+O)$ and $(E+O)D_{0.20}(E+O)$. The mild conditions of the $(E+O)(E+O)$ sequence yielded 43% delignification for both 2 and 10 kg/ton of black liquor carryover and 35% delignification with no carryover. The increase in delignification with the addition of black liquor is presumably due to residual alkali left in the carryover [12, 21-23]. The use of a low charge of ClO_2 and splitting the caustic charge between two $(E+O)$ stages significantly improved the response of the pulp toward delignification in the second $(E+O)$ stage, as was also reported by Chakar et al.[6] However, the increase in delignification compared to the $(E+O)(E+O)$ sequence was 6% and 10% for the 2 and 10 kg/ton carryover levels, respectively, while an 18% increase in delignification is apparent for pulp having interstage washing and no carryover. This effect is presumably due to partial consumption of ClO_2 by the black liquor carryover,

thereby decreasing the overall efficiency of this bleaching agent. The delignification response using 10 kg/ton carryover was often lower than that of a 2 kg/ton black liquor carryover charge. It would seem reasonable that this decreased delignification can be attributed to an increase in the total number of competing reactions between pulp lignin and dissolved material in the black liquor.
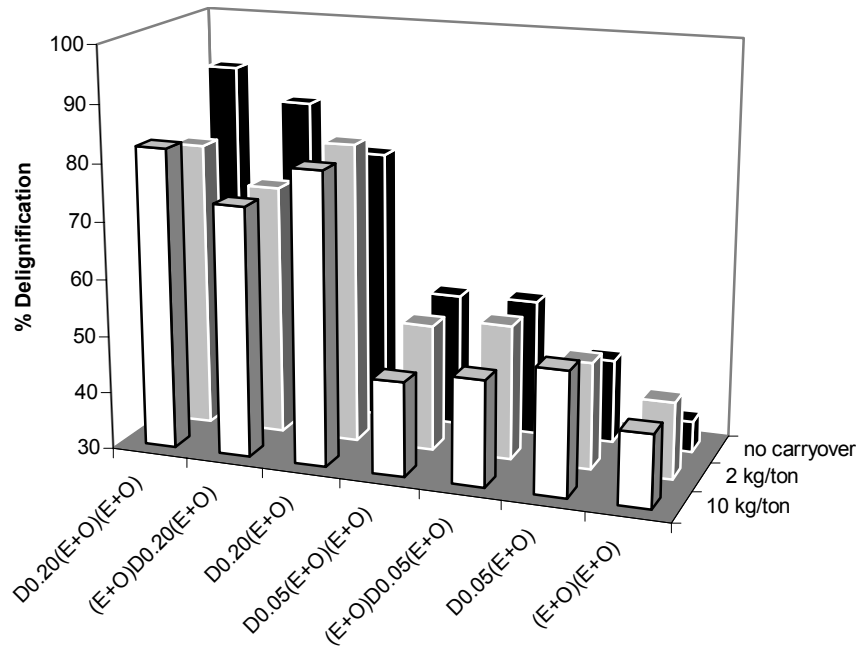
Figure III.1. Mini oxygen delignification responses for a 26.3 kappa SW kraft pulp with no carryover, 2 kg/ton carryover, and 10 kg/ton carryover. The pulps having no carryover involved interstage washing while the pulps having added carryover involved no interstage washing.

The viscosity losses for the no carryover, 2 kg/ton, and 10 kg/ton carryover SW kraft pulps are summarized in Figure III.2. The initial viscosity of this pulp was 33.2 cP. As expected, the viscosity loss for the $D_{0.05}(E+O)(E+O)$ sequence is smaller than that for the $(E+O)D_{0.05}(E+O)$ sequence due to the placement of the first (E+O) stage in the sequence. Interestingly, the viscosity losses increased as a function of the amount of carryover in the pulp. It is anticipated that black liquor carryover introduces transition metal ions to the pulp. These transition metal ions can then form radicals, leading to degradation of the carbohydrates. The $(E+O)D_{0.05}(E+O)$ sequence yielded a greater viscosity loss than the $(E+O)(E+O)$ sequence, although it provided improved delignification. This could be attributed to the selectivity of the intermediate chlorine dioxide stage.
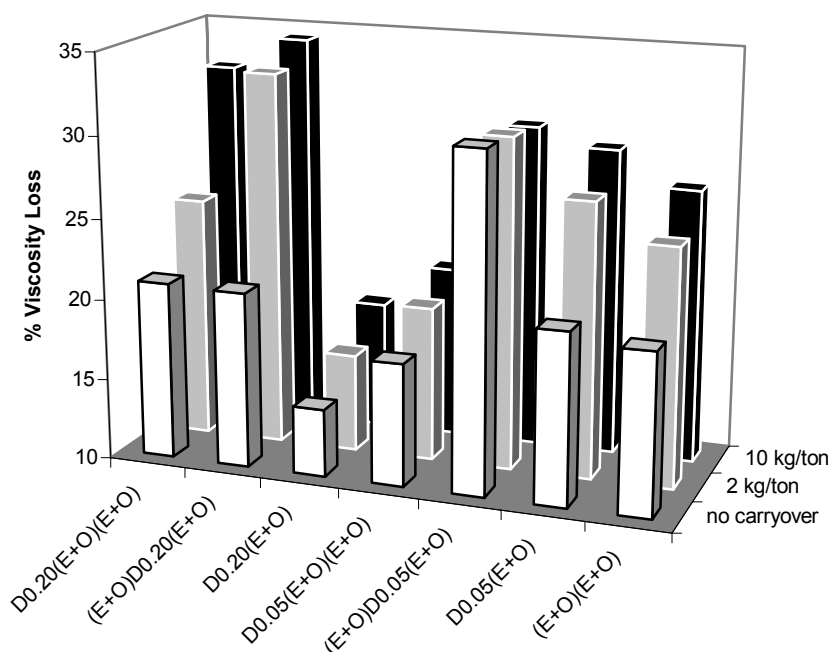
Figure III.2. Mini oxygen delignification pulp viscosity losses (%) for a 26.3 kappa SW pulp with no carryover, 2 kg/ton, and 10 kg/ton black liquor carryover. The pulps having no carryover involved interstage washing while the pulps having added carryover involved no interstage washing.

Figure III.3 presents the selectivity (defined as Δkappa/Δviscosity) data for the no carryover, 2 kg/ton, and 10 kg/ton carryover SW kraft pulps. In general, the selectivity decreases as a function of black liquor carryover load. This observation is contrary to results reported by others.[19-22] However, the conditions used in those studies indicate that much higher levels of carryover were used. In addition, the carryover used in those studies may have been model compounds or black liquor with low metals content. The selectivity of the $(E+O)D_{0.05}(E+O)$ sequence is much lower than that for the $D_{0.05}(E+O)(E+O)$ sequence, due primarily to the large change in viscosity that was brought about by the placement of the $(E+O)$ sequence. As a result, the selectivity of the $(E+O)D_{0.05}(E+O)$ sequence is comparable to that of a $(E+O)(E+O)$ sequence. Meanwhile, the sequences involving high kappa factor D stages were the most selective of this study, due to their high delignification compared to the other sequences employed in this study.
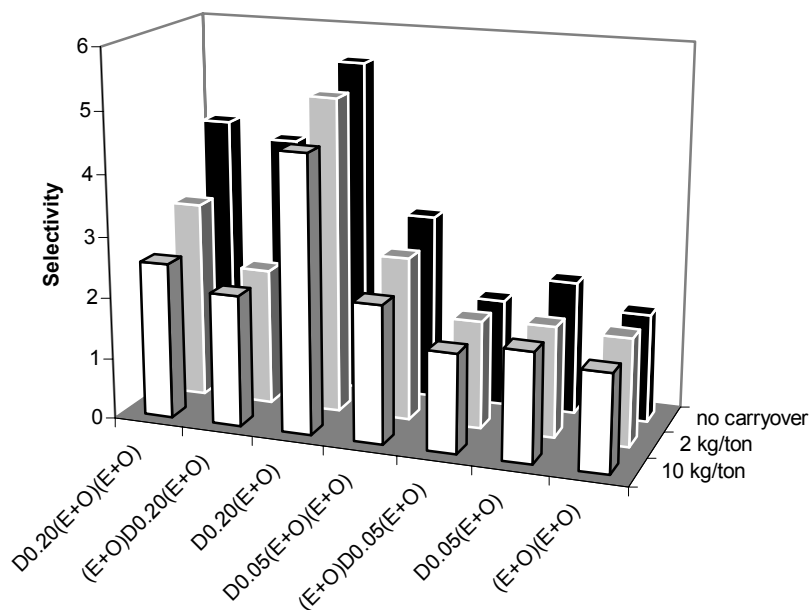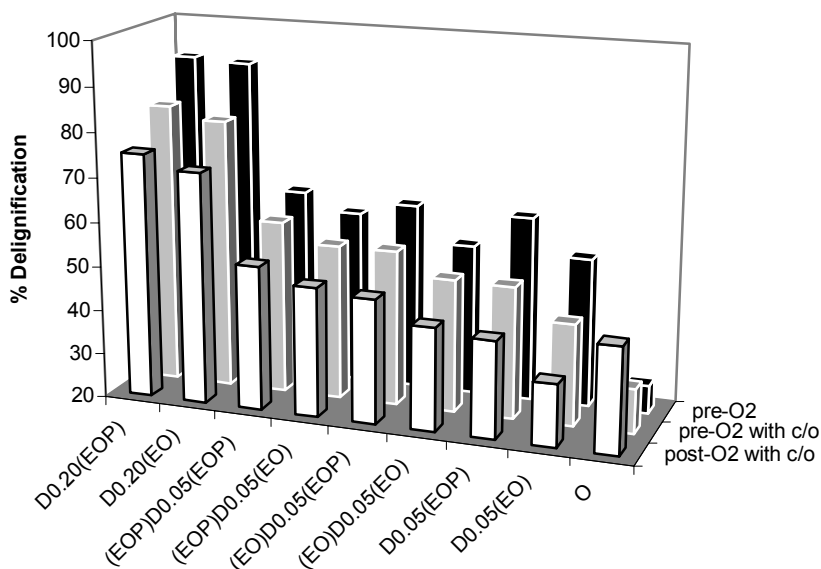
Figure III.3. Mini oxygen delignification selectivity (Δkappa/Δviscosity) of SW kraft pulp with no carryover, 2 kg/ton, and 10 kg/ton black liquor carryover. The pulps having no carryover involved interstage washing while the pulps having added carryover involved no interstage washing.

Mini O Reinforced with H_2O_2. In an effort to further enhance a poor man's oxygen stage, this study was extended to investigate the impact of black liquor carryover on a mini oxygen delignification system reinforced with hydrogen peroxide for both pre- and postoxygen delignified SW kraft pulps. The consistency of all the stages was maintained at 10% while a constant charge of magnesium sulfate in the mini oxygen stages was employed to minimize the number of experimental variables. The mini oxygen delignification studies were maintained at an oxygen pressure of 90 psi and were stirred at a constant rate throughout the experiment. Black liquor was added to the pulp at only one level, 10 kg solids per o.d. ton of pulp. There was no interstage washing employed in any of the studies employing black liquor carryover. These results were then compared to control studies that did not employ any black liquor or bleach plant effluent.

The delignification response for the preoxygen with no carryover as well as the pre- and postoxygen delignified SW kraft pulps with 10 kg/ton of black liquor carryover is summarized in Figure III.4. The kappa 26.3 pre-O_2 pulps with no black liquor carryover exhibited a greater extent of delignification than the kappa 24.2 pre-O_2 pulps with carryover, as was also observed in our earlier study. In addition, the 24.2 kappa pre-O_2 pulp exhibited a greater extent of delignification than that of the 8.9 kappa post-O_2 pulp except in the case of the O_2 treatment. This effect is presumably due to the nature of the residual lignin in the post-O_2 pulp. This lignin is further oxidized than the lignin in the pre-O_2 pulps and is thus more resistant to additional oxidation. The extent of delignification was proportional to the amount of hydrogen peroxide in the bleaching

sequence. As the hydrogen peroxide was decreased, the extent of delignification also decreased. It is interesting to observe the differences in delignification for the $(E+O+P)D_{0.05}(E+O)$ and $(E+O)D_{0.05}(E+O+P)$ sequences. Although there was a difference observed in delignification for these two sequences for the pre-O_2 pulps with no carryover, there was no apparent difference for either the pre- or post-O_2 pulps having added black liquor carryover. This further suggests that there are competing reactions occurring between the pulp lignin and dissolved material in the black liquor, thereby leading to a lower bleaching effectiveness.

Figure III.4. Delignification responses (%) for a pre-O_2 pulp with no black liquor carryover and a pre-O_2 and post-O_2 SW kraft pulp with 10 kg/ton of black liquor carryover. The pulps having no carryover involved interstage washing while those having added carryover employed no interstage washing.

The changes in pulp viscosity for the 27.4 cP pre-O_2 pulps with no carryover as well as the 26.5 cP pre-O_2 and 21.0 cP post-O_2 SW kraft pulps with 10 kg/ton of black liquor carryover are summarized in Figure III.5. Although the extent of delignification increased with greater amounts of hydrogen peroxide, the loss in viscosity is also greater for increasing amounts of hydrogen peroxide. This effect is presumably due to the decreased selectivity of hydrogen peroxide under increased oxygen pressure. In general, a greater viscosity loss was observed for both pre-O_2 pulps when compared to that for the post-O_2 pulps. It is interesting to observe that the viscosity loss was often greater for the pre-O_2 pulps with no carryover than for the pre- and post-O_2 pulps with added carryover. This effect further reinforces the theory that there are competing reactions between pulp lignin and the dissolved material in the black liquor.[17,18] The black liquor may indirectly protect the carbohydrates from degradation by providing these competing reaction pathways. However, this effect was not observed for the post-O_2 SW kraft pulp treated with another oxygen stage.
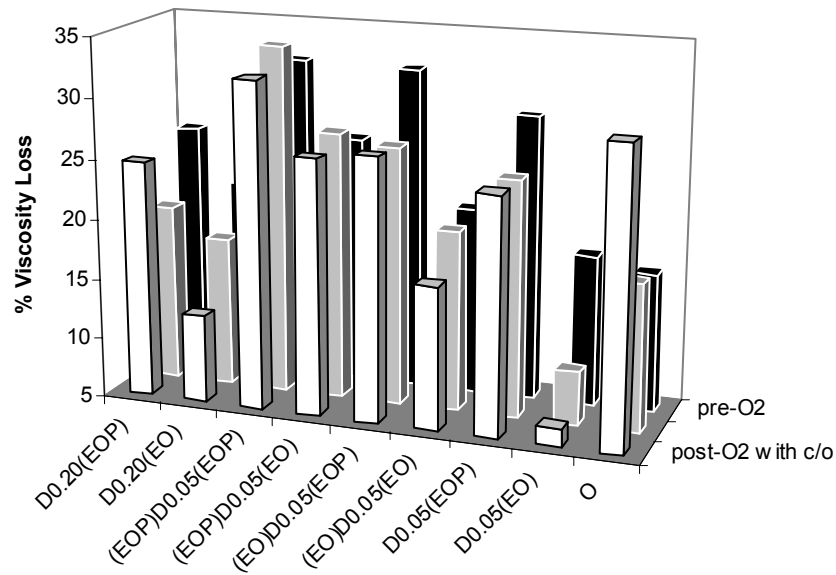
Figure III.5. Viscosity losses (%) for a 27.4 cP pre-O_2 pulp with no black liquor carryover and a 26.5 cP pre-O_2 and 21.0 cP post-O_2 SW kraft pulp with 10 kg/ton of black liquor carryover. The pulps having no carryover involved interstage washing while those having added carryover employed no interstage washing.

Figure III.6 presents the selectivity (defined as Δkappa/Δviscosity) data for the pre-O_2 pulps with no carryover and the pre- and post-O_2 SW kraft pulps with black liquor carryover. In general, the selectivity decreased when comparing the pre-O_2 pulps with no carryover to the pre-O_2 pulps with 10 kg/ton carryover. This effect is presumably due to the extent of delignification outweighing the viscosity loss for the pulps with no black liquor carryover. In addition, the selectivity decreased when comparing the pre-O_2 pulps with carryover to that of the post-O_2 pulps with carryover. The reason for this is presumably due to the nature of the residual lignin. The residual lignin remaining in the post-O_2 pulps may be more difficult to oxidize than the residual lignin in the pre-O_2 pulps, thereby reducing the overall selectivity. An exception to this is observed in both the $D_{0.20}(E+O)$ and $D_{0.05}(E+O)$ sequences. These short sequences actually improved the selectivity of the post-O_2 over the pre-O_2 pulps with carryover and without carryover.

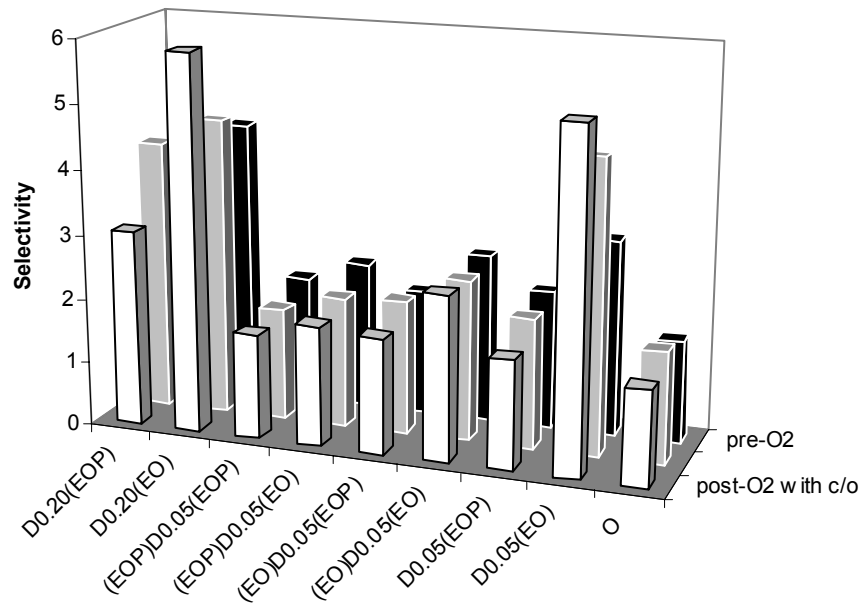**Figure III.6.** Selectivity responses for a pre-O$_2$ pulp with no black liquor carryover and a pre-O$_2$ and post-O$_2$ SW kraft pulp with 10 kg/ton of black liquor carryover. The pulps having no carryover involved interstage washing while those having added carryover employed no interstage washing.

The changes in brightness for the pre-O$_2$ pulps with no carryover as well as the pre-O$_2$ and post-O$_2$ SW kraft pulps with 10 kg/ton of black liquor carryover are summarized in Figure III.7. The changes in brightness follow trends similar to the delignification responses illustrated earlier. The kappa 26.3 pre-O$_2$ pulp with no black liquor carryover exhibited a greater brightness change for all treatments than the kappa 24.2 pre-O$_2$ pulp with carryover. In addition, the 24.2 kappa pre-O$_2$ pulp exhibited a greater brightness change than the 8.9 kappa post-O$_2$ with the exception of the O$_2$ treatment. It is interesting to observe that the brightness change was based on the exiting bleaching stage. This observation is most notable in the sequences involving three stages. Those sequences ending with an (E+O+P) stage often increased the brightness compared to those ending in an (E+O) stage, presumably due to the ability of the hydrogen peroxide to react with and destroy chromophores remaining in the pulp.
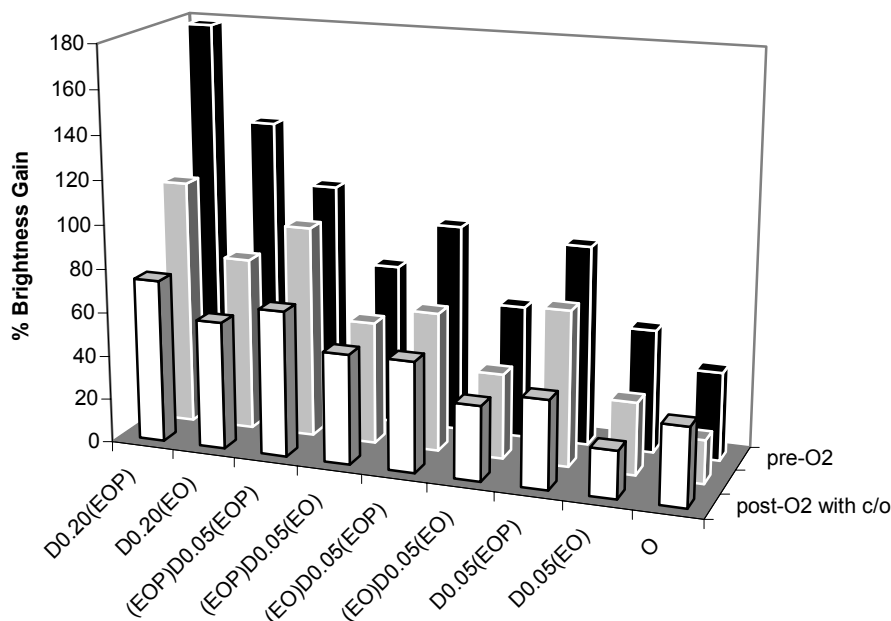
Figure III.7. Changes in brightness(%) for a pre-O_2 pulp with no black liquor carryover and a pre-O_2 and post-O_2 SW kraft pulp with 10 kg/ton of black liquor carryover. The pulps having no carryover involved interstage washing while those having added carryover employed no interstage washing.

Chapter III. Conclusions

The mini oxygen delignification studies with black liquor carryover confirmed that using a poor man's O to remove lignin from kraft pulps continues to be a promising technology. Analysis of the mini O_2 systems indicated that these technologies had superior performance with pre-O_2 pulps when compared to post-O_2 SW kraft pulps. Furthermore, these studies confirmed the proposed benefits of splitting the charge of the mini O in two and further oxidizing the pulp with a low kappa factor chlorine dioxide stage. Analysis of the mini oxygen systems reinforced with hydrogen peroxide revealed that the addition of hydrogen peroxide in the last stage of a (E+O)D(E+O) sequence had a greater impact on bleaching performance than if placed in the front of the sequence. These studies also confirmed that black liquor carryover has little or no effect on the final pulp physical properties. However, the modest levels of black liquor carryover employed in this study may not be entirely indicative of an actual bleach plant. Hence, future studies within our research group will address this issue and will be reported in the near future.

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Chapter IV. Extending the Limits of Oxygen Delignification for O, OO and Mini-O Stages

This phase of the research program was directed at using an O stage to improve overall pulp yields for US wood resources 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 and hardwood > 15. The overall wood savings following this approach has been reported to be in the range of 2 – 6% for a modern pulp mill.[1] 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.[2] have reported improved selectivity with an extended oxygen OO system on high kappa kraft pulps. Employing kraft pulps with a kappa number of 40 or greater, it was demonstrated that an OO system can increase pulp yields ≈ 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.[3]

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.[4] 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.[5]

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, Gellerstedt, and others into the chemistry of oxygen delignification have certainly detailed how phenolic lignin-like structures can be oxidized under an O stage.[6,7,8] Typically, oxidative reactions involve the loss of an electron from the phenolate anion to oxygen and subsequent attack of the phenolate radical by oxygen as described in the introduction.

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.[9] 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.,[10] Moe and Ragauskas,[11] and Asgari and Argyropoulos[12] 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[13] and Lachenal et al. [14]

This study examined 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.

Chapter IV. Experimental

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 chapter. 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.[15] Table IV.1 summarizes the results of ICP analysis.

Table IV.1. Metal analysis of kraft brownstocks.

Metal	Low Kappa SW Kraft Brownstock	High Kappa SW Kraft Brownstock
Na	720	884
K	359	88
Mg	315	727
Ca	2590	1990
Mn	33	57
Fe	70	18
Ni	1	1

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.[16] 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 IV.2 summarizes the delignification conditions.

Table IV.2. Oxygen bleaching conditions.[a]

Stage	O_2 Pressure/psi	NaOH[b] L - H	Temp. /°C	Time/min.
O	80	1.5 - 2.5 2.5 - 4.1 3.5 - 5.8	105	80
OO	i) 130 ii) 60	1.5 - 2.5 2.5 - 4.1 3.5 - 5.8	i) 80 ii) 105	i) 20 ii) 60
(E+O)D[c](E+O)	80	1.5 - 2.5 2.5 - 4.1 3.5 - 5.8	80	20

[a]$MgSO_4$ charge: 0.30%; Consistency: 12%; [b]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; [c]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 ClO_2, 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 um-246.[17] 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[17] 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 H_2SO_4. 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.[18] 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 ultracentrifuge, 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.

^{13}C NMR Analysis of Residual Lignin: Quantitative ^{13}C 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.[18] The NMR experiments were performed at 50°C on samples containing 150-300 mg lignin/ml of DMSO-d_6. 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.

^{31}P 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[18] and analyzed by ^{31}P NMR.

Chapter IV. Results and Discussion

Oxygen Bleachability of Kraft Pulps: Previous studies reported by Moe and Ragauskas[11] 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.[2,3] To minimize the number of experimental variables, the consistency of all O stages was maintained at 12% and a constant charge of $MgSO_4$ was employed. The oxygen pressure was maintained at 80 psi for all studies except for the OO experiments. This later sequence required an initial O_2 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 IV.1. 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 ClO_2 (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.
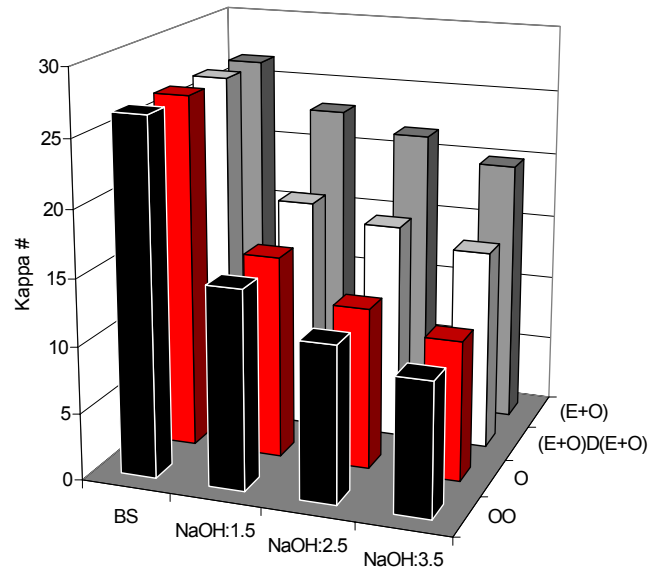
Figure IV.1. Changes in kappa number for low lignin content SW kraft pulp before and after O, OO, (E+O), and (E+O)D(E+O).

An examination of the extent of delignification for the high kraft pulps (Figure IV.2) 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.
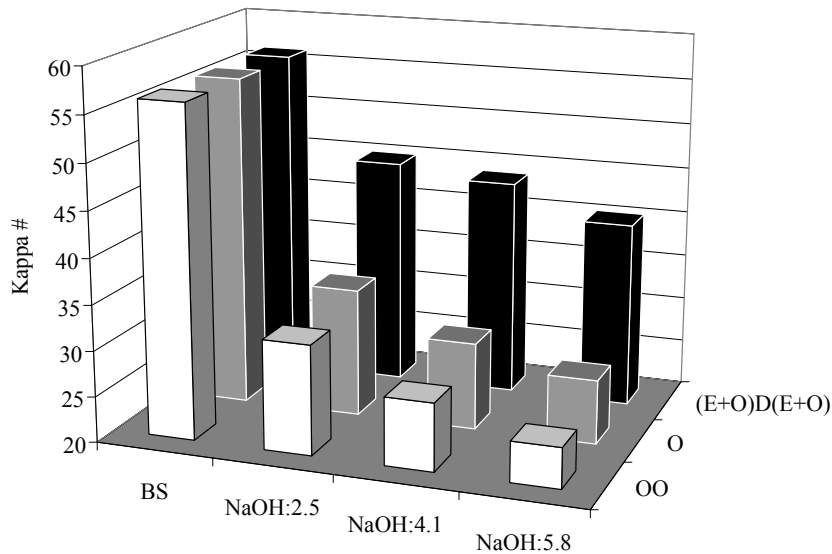
Figure IV.2. Changes in kappa number for high lignin content SW kraft pulp before and

after O, OO, and (E+O)D(E+O).

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 IV.3.
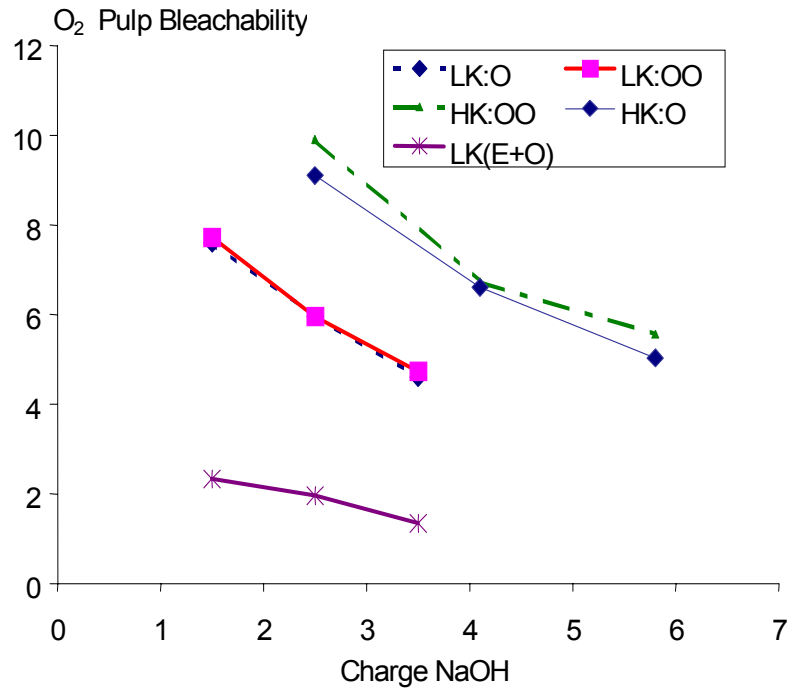
Figure IV.3. Pulp bleachability of 26.6 (LK) and 56.2 (HK) kappa SW kraft pulps for O, (E+O), and OO.

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 ClO_2.

The changes in pulp viscosity for the high and low kappa pulps for O, OO, and (E+O)D(E+O) are summarized in Figure IV.4.
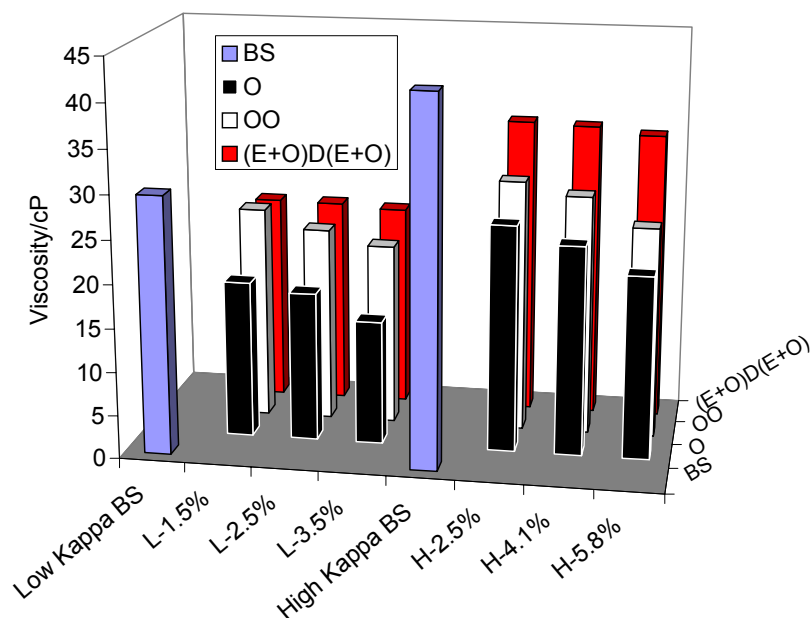
Figure IV.4. Pulp viscosities (cP) for brownstocks BS), O, OO, and (E+O)D(E+O) high (H) and low (L) kappa kraft pulps.

Although the O and OO sequences yielded relatively comparable amounts of delignification for the low kappa pulp, the OO exhibited improved viscosities. Interestingly, the sequence $(E+O)D_{kf:0.05}(E+O)$ 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 OO stage is clearly superior with respect to delignification and viscosity retention. Comparison of the viscosity changes for the low and high kappa pulps can not be solely attributed to lignin and pulp carbohydrates given the differences in metal content for the two pulps (see Table IV.1).

Pulp 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 IV.5 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.
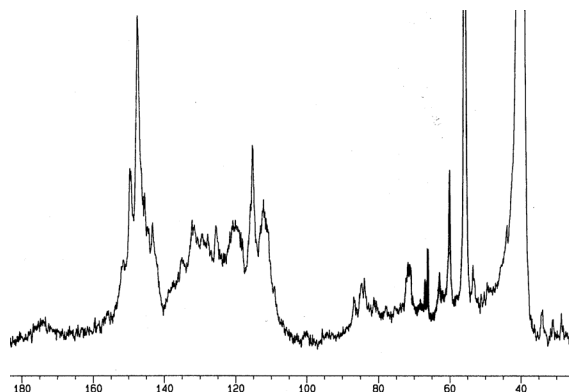
Figure IV.5. Quantitative ^{13}C NMR analysis of residual lignin from high kappa kraft brownstock.

Table IV.4 Residual lignin functional group analysis via ^{13}C NMR[a]

Brownstock	High Kappa	Low Kappa
$\underline{C}H_2Ph$	0.03	0.09
$\underline{Me}O\text{-}Ph$	0.89	0.81
Cβ in ββ and Cβ in β-5	0.14	0.13
Cγ in β-O-4	0.32	0.27
Aromatic $\underline{C}$-R : Aromatic $\underline{C}$-H	1.96:1.00	2.05:1.00
Acid	0.17	0.31

[a]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.[19,20] The increased content of diphenyl methane units and the changes in aromatic substituted carbons ($\underline{C}$-R):aromatic unsubstituted hydrogen 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 C5-noncondensed phenolics:C5-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.

Low Kappa Pulp	High Kappa Pulp
Conventional O, 1.5 and 3.5% NaOH	Conventional O, 2.5 and 5.8% NaOH
(E+O)D(E+O), 3.5% NaOH	(E+O)D(E+O), 5.8% NaOH
OO, 3.5% NaOH	OO, 5.8% NaOH

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 $(E+O)D_{kf:0.05}(E+O)$ 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 IV.6 and .7.

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.
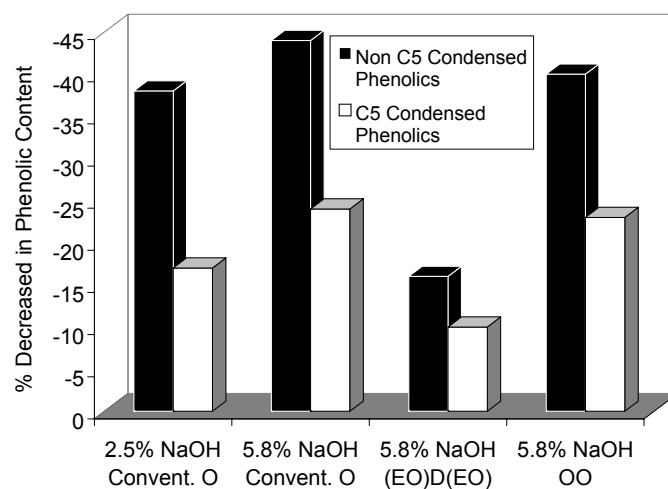
Figure IV.6. Changes in phenoxy content of recovered effluent lignins after treatment of low kappa SW kraft pulp with O, OO, and (EO)D(EO). Brownstock pulp had a C5 noncondensed, C5 condensed phenoxy content of 0.88 and 0.82 mmol/g of lignin, respectively.

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.
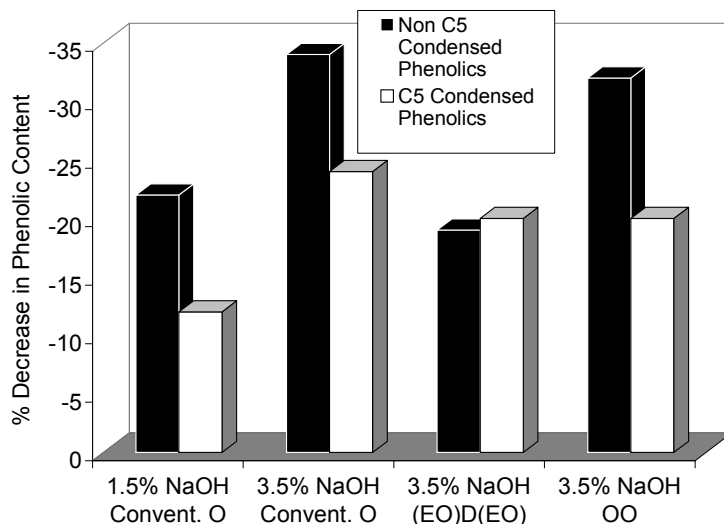
Figure IV.7. Changes in phenoxy content of recovered effluent lignins after treatment of high kappa SW kraft pulp with O, OO, and (EO)D(EO). Brownstock pulp had a C5 noncondensed, C5 condensed phenoxy content of 0.84 and 0.73 mmol/g of lignin, respectively.

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 ($\cong 0.07$ 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.

Chapter IV. Conclusion

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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Chapter V: Controlling the Efficiency of Oxygen Delignification though Selected Oxygen Delignification via Pulp Mixing and Metals Management

Although the chemical structure and reactivity of residual lignin play a role in its effective removal during oxygen delignification, mill-defined operational parameters may play an equally important role in governing the extent of lignin removal during this process. Mass transfer of oxygen was identified as one of the important factors affecting the efficiency of oxygen delignification.[1,2,3] Nonprocess elements are also suspected to strongly affect the oxygen delignification process. Among these, iron and copper are reportedly able to induce the generation of harmful radicals that create a detrimental effect on the pulp viscosity,[4] whereas magnesium is presumed to be beneficial.

First, it is generally accepted that the reaction between oxygen and residual lignin requires a three-phase transfer step: it involves the transfer of oxygen from gas to liquid and then to solid.[5] Since mixing distributes oxygen more uniformly throughout the suspension, it can reduce the diffusion path of oxygen and facilitate mass transfer.[6]

It was found, for example, that the oxygen delignification of a hardwood kraft pulp steadily increased with mixing speeds in the range of 0 to 3000 rpm.[7] This work demonstrated that mixing at 3000 rpm for 10 seconds after the injection of oxygen results in an increase in delignification of 4.3% versus a control. Similarly, Yaldez[6] reported that a change of mixing intensity from 310 rpm to 1425 rpm increased delignification by an additional 15%. This substantial improvement was attributed to pulp fluidization. However, high-speed, short-time mixing is not the only means to improve oxygen delignification. Hsu and Hsieh[8] demonstrated that continuous mixing throughout an oxygen delignification run at 300 rpm could achieve better delignification than mixing at 1000 rpm for 1 minute at the beginning of bleaching.

It is expected that intensive mixing may cause mechanical damage to the fibers from the strong shear force applied to the pulp. Reeve and Earl[9] reported that the freeness of delignified pulp decreased after the sample was fluidized for ten seconds. However, Yaldez and Stark[6] indicated that no such pulp-beating effect could be observed.

Not only does pulp mixing affect the performance of the oxygen stage, but a variety of metal ions that either originate in the pulp or are introduced during the reaction may influence the performance of an O-stage. In order to minimize the degradation of pulp carbohydrates from metal ion-induced radical reactions, it is essential to understand the roles of the major metal ions in the system. It was demonstrated that peroxides are generated in oxygen delignification from phenolic lignin structures[10] and carbohydrate components.[11] In the presence of metal ions, oxygen generated peroxides are decomposed and likely form radical species.[12] The hydroxyl radical was identified as a strong oxidative species capable of attacking both lignin and carbohydrate.[13] Although the reactions between lignin and hydroxyl radicals facilitate lignin degradation, the oxidation of the carbohydrates may lead to the formation of C_2 or C_3 carbonyl groups.[14]

These oxidized cellulose/hemicellulose sites can result in an alkaline-catalyzed chain via a β-elimination reaction yielding reduced pulp viscosity.

The protective nature of magnesium has long been known but is not completely clear. Several hypotheses were proposed to account for its positive effect including: (1) formation of stable peroxide complexes;[15] (2) deactivation of the transition metal ion by absorption[16] or by formation of complexes; (3) formation of complexes with carbonyl group in C2 or C3 position of a glucose unit and thus being able to eliminate further degradation.[16]

As part of the work in the study of extended oxygen delignification, this research evaluates the limitation of mixing in oxygen delignification on softwood kraft pulp in terms of lignin removal, pulp viscosity, and freeness change. In addition, the influence of metal ions on the oxygen delignification of both softwood and hardwood kraft pulps was evaluated in terms of delignification selectivity. The metal ion profiles were manipulated by chelation, acid washing, and addition of magnesium sulfate.

Chapter V. Results and Discussion

Removal of Metal Ions by EDTA Treatment

EDTA chelation of metals in a softwood (SK) and a hardwood kraft pulp (HK) was performed in this study to establish a baseline for its effect on metals management during oxygen delignification. The pulp samples were subjected to EDTA-chelation followed by a complete washing to remove the metal ions in the pulps (all conditions are detailed in the accompanying experimental section). The metal profiles of the pulp samples before and after EDTA treatment are shown in Table V.1.

Table V.1. Metal ions profiles (ppm) of pulp samples pre- and post-EDTA stage. (SK = softwood kraft, HK = hardwood kraft, Q = chelation stage)

Samples	Mn	Fe	Cu	Co	Mg	Ca
SK	95.3	7.32	0.8	Trace	311	890
HK	15.4	42.5	24.0	Trace	222	1945
QSK	0.3	3.7	0.4	Trace	163	136
QHK	0.7	13.9	1.5	Trace	103	460

As compared to softwood kraft pulp, the hardwood kraft pulp sample contained less manganese and magnesium, but more copper and iron. After EDTA treatment the manganese in the pulps was drastically reduced by more than 95%, whereas magnesium was reduced by approximately 50%. The reduction levels for iron and copper are between the reductions observed for the manganese and magnesium. The difference in the chelation efficiency for the ions is attributed, in part, to their ability to form complexes with EDTA. For example, as demonstrated by Lapierre[17] the magnesium ion has a lower tendency to form complexes with EDTA than does the ferric ion.

Judging from the formation constant of iron-EDTA complexes (K_{eq}), iron should be removed by EDTA efficiently.[16] However, the data in Table V.1 indicate that there are still significant amounts of iron left in the pulp after EDTA treatment. The failure to completely remove this metal ion may be due to the intimate connection iron has with fiber components. Although most of the iron in a tree is found in the root, bark, and leaf studies with modern analytical techniques indicate that wood xylem also contains iron, which mainly concentrates in the regions of the torus and half-bordered pit membrane.[18] After chemical pulping, iron may exist in the pulp as a complex with the carbohydrates[19] and lignin.[20] These structural components undoubtedly compete with EDTA for complexing iron and limit its removal from the pulp during the Q-stage.

Influence of Metal Chelation on Oxygen Delignification

In order to evaluate the effect of the metal ion profile on the efficiency of oxygen delignification, the SW and HW kraft pulps after EDTA-chelation were subjected to oxygen delignification with and without the addition of magnesium sulfate. As indicated in Figure V.1, the hardwood kraft pulp after EDTA treatment displays lower delignification than that without the pretreatment (55.1% vs. 57.1%). Similarly, the addition of magnesium sulfate also results in a lower lignin removal than the control (52.1% as compared with 57.1%).
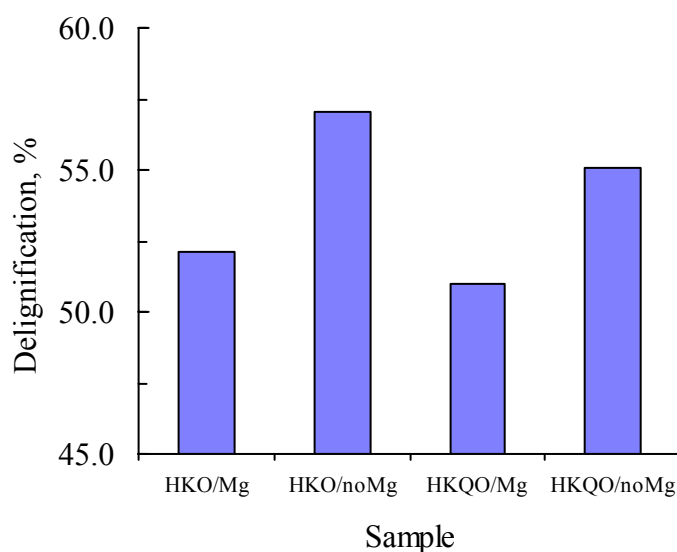
Figure V.1. Influence of EDTA treatment and addition of magnesium sulfate on the oxygen delignification of hardwood kraft pulps. (HK: hardwood kraft, Q: EDTA treatment; Mg: addition of 0.0 and 0.05% magnesium sulfate. O: oxygen delignification with 1.5% NaOH and 10% consistency at 90 psi oxygen and 100°C for 1 hr.)

As indicated in Figure V.2, oxygen delignification of the hardwood pulp after EDTA treatment resulted in a 8.6% reduction in pulp viscosity, whereas in the case of the untreated sample a 15.5% viscosity reduction was found.
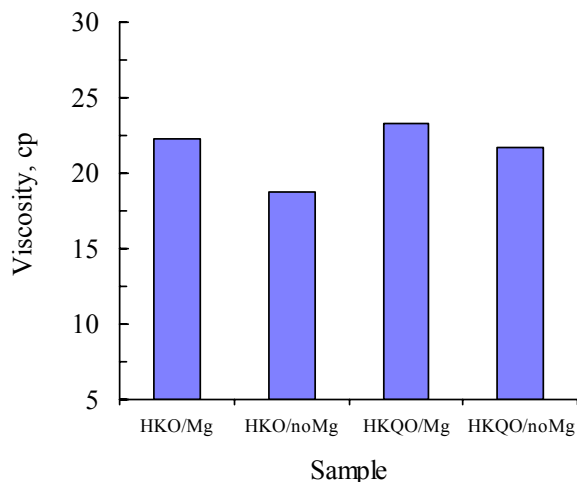
Figure V.2. Influence of EDTA treatment and addition of magnesium sulfate on pulp viscosity after oxygen delignification (symbols and conditions are the same as in Fig. III.1).

The addition of 0.05% magnesium sulfate was found to substantially reduce the viscosity losses from 29.2% to 15.5%. It is evident from these results that the removal of metal ions or the addition of magnesium sulfate can retard carbohydrate degradation. However, the price for the maintenance of pulp viscosity is the reduction in delignification. This observation is in agreement with the basic mechanistic aspects of oxygen delignification. The presence of metal ions is known, for example, to induce the generation of hydroxyl radicals, which attack lignin and pulp carbohydrates. The amounts and types of metals in the pulp can clearly influence both delignification and carbohydrate degradation.

The effect of chelation and magnesium addition on the oxygen delignification of softwood kraft pulp is illustrated in Figures V.3 and V.4. As indicated, the results are generally in the same trend as delignification of hardwood pulps. The removal of metal ions and the addition of magnesium sulfate lead to a lower extent of delignification and higher pulp viscosity.

Figure V.3. The effect of EDTA treatment and addition of magnesium sulfate on the oxygen delignification (Symbols are the same as in Figure III.1. Oxygen delignification was conducted with 2.5% NaOH and 10% consistency at 100°C and 90 psi oxygen for 1 hr.)
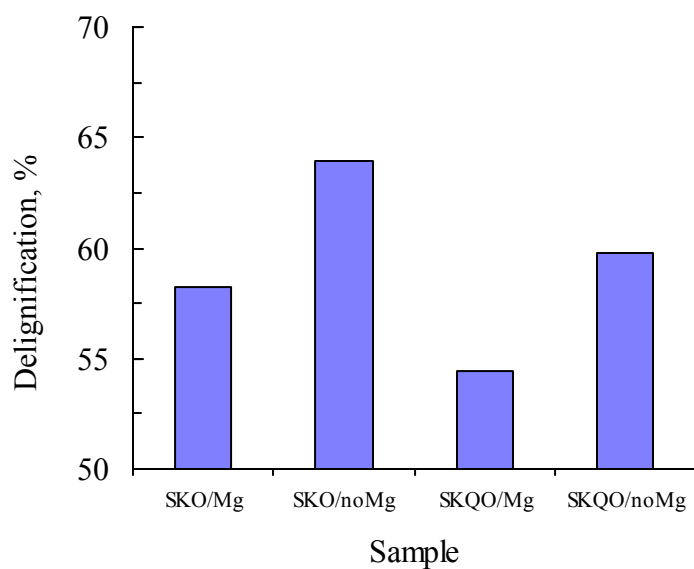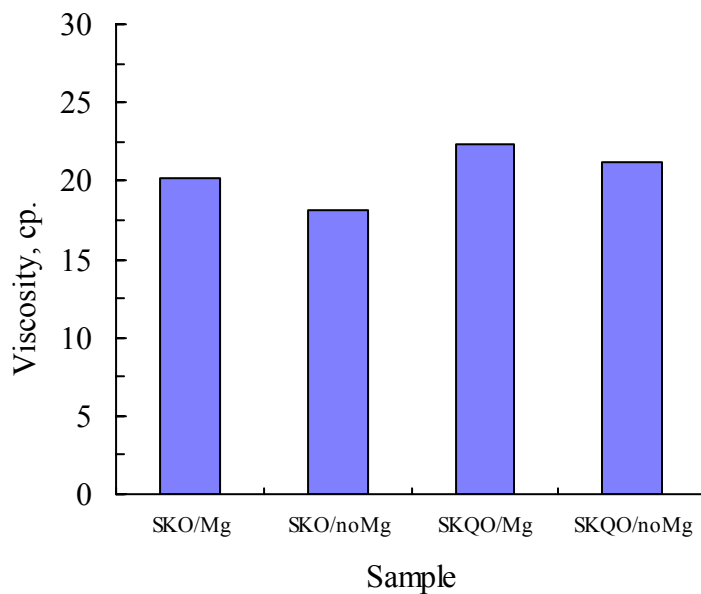

Figure V.4. Influence of EDTA treatment and addition of magnesium sulfate on pulp viscosity after oxygen delignification. (Symbols and oxygen delignification conditions are the same as in Figure III.3)

The original softwood kraft pulp has a more sensitive response to the addition of magnesium in terms of viscosity maintenance than the EDTA-treated brownstock. O-

delignification of SW kraft pulp without a prior EDTA treatment employing a 0.05% MgSO$_4$ charge resulted in 11.6% higher pulp viscosity than the control experimental employing no MgSO$_4$. Whereas in the case of EDTA-treated pulp, only a 5.2% increase in pulp viscosity was obtained when a 0.05% charge of MgSO$_4$ was employed. The comparable results were observed for the hardwood kraft pulp. A 19.3% higher viscosity was obtained from the addition of magnesium sulfate in the oxygen delignification of the untreated sample, whereas the increase was reduced to 7.4% in the bleaching of EDTA-treated pulp. This difference presumably arises from the reduction of metal ions by EDTA treatment, which causes the magnesium addition to be less significant for the protection of the pulp carbohydrates.

Effect of Magnesium Levels on O-Delignification Selectivity

Figures V.5 and V.6 illustrate O-delignification selectivity of a hardwood and a softwood kraft pulp, respectively. As indicated, although the addition of magnesium sulfate in the oxygen bleaching of the softwood kraft pulp leads to a higher selectivity than the control (Figure V.5), the improvement in selectivity is less significant as compared to the oxygen bleaching of the hardwood kraft pulp (Figure V.6).
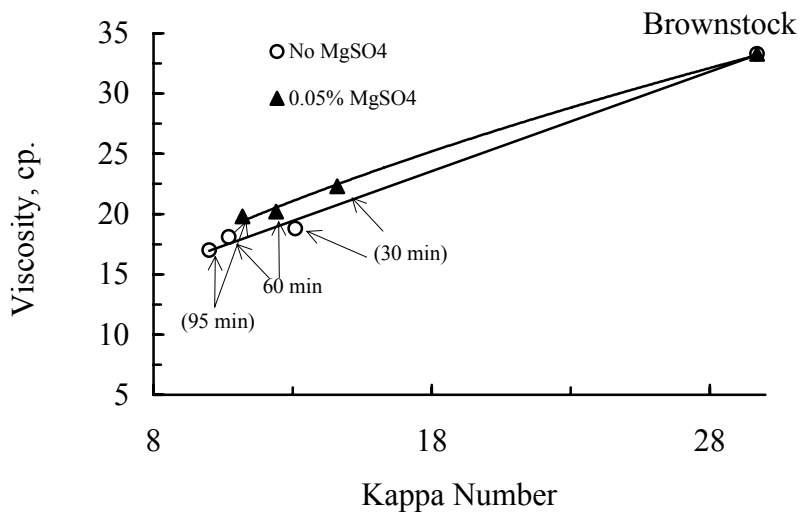
Figure V.5. Influence of added magnesium sulfate on delignification selectivity of softwood pulp (Magnesium sulfate addition: 0.00 or 0.05%. Oxygen bleaching with 2.5% NaOH and 10% consistency at 100°C and 90 psi O$_2$ for 30, 60, and 95 min.).
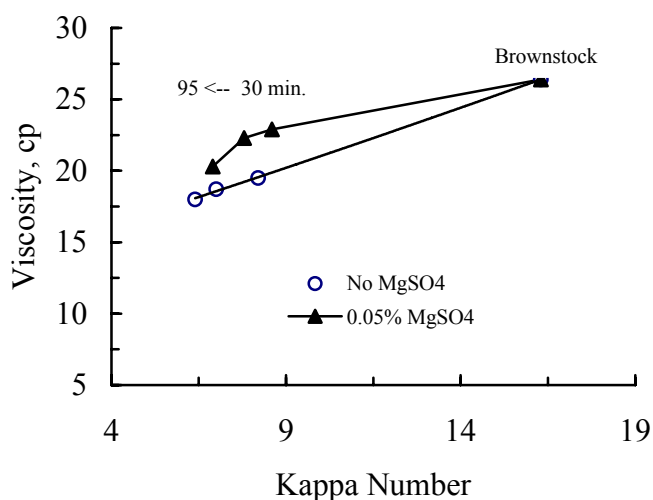
Figure V.6. Influence of added magnesium sulfate on delignification selectivity of the hardwood pulp (The conditions for the oxygen delignification are the same as in Figure III.5 except 1.5% NaOH was used).

This difference in selectivity was attributed to the different NPE profiles in the original pulps. As indicated in Table III.1, the softwood pulp (SK) contains high magnesium and low iron and copper. Because magnesium is beneficial, whereas iron and copper are harmful for the maintenance of pulp viscosity, the favorable metal ion profile in the softwood pulp thus makes the addition of extra magnesium sulfate less important. In contrast, the hardwood pulp contains high amounts of iron and copper and a low content of magnesium; thus, the addition of magnesium is important to reach a better delignification selectivity. Consequently, a significant improvement in selectivity was observed when magnesium sulfate was added in the oxygen delignification of this hardwood pulp.

Interestingly, there are also inconsistent reports on the selectivity improvement by magnesium sulfate addition in industrial applications. Some mills have reported that little difference in delignification selectivity was observed by the addition of magnesium sulfate in the oxygen bleaching of hardwood pulp, whereas others have claimed that magnesium additives are important to maintain a high pulp viscosity.

To verify the influence of native magnesium on oxygen bleaching, two additional hardwood kraft pulps (HKA and CHK with initial kappa number of 13.7 and 17.5 respectively, see experimental for details) having different magnesium contents were subjected to oxygen delignification. Delignification selectivity was determined by plotting pulp viscosity vs. kappa number. Table III.2 displays the basic metal ions profile of the two pulp samples. As compared to HKA, CHK (Commercial Hardwood) pulp contained much higher magnesium levels.

Table V.2. Metal ion profiles (ppm) of two hardwood kraft pulps.

Sample	Mn	Fe	Cu	Co	Mg	Ca
HKA	10.1	5.4	19.4	trace	230	4090
CHK	45.4	18.5	0.6	trace	647	3310

The response of these two pulps under standard O-delignification conditions is summarized Figures V.7 and V.8.

As expected, HKA exhibited a higher response in delignification selectivity against the addition of magnesium sulfate compared to the CHK sample. The results indicate that the native magnesium in pulp plays a similar role to the added magnesium sulfate during oxygen bleaching.
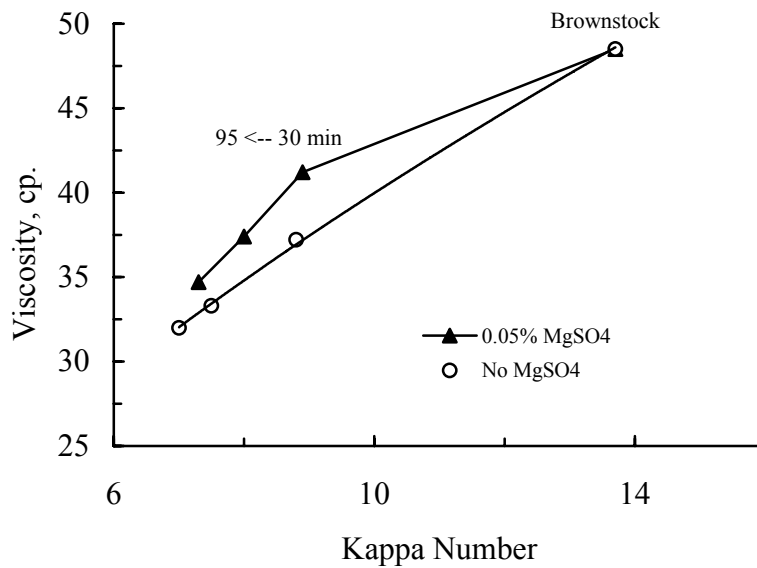
Figure V.7. Influence of added magnesium sulfate on delignification selectivity of HKA pulp (Oxygen bleaching with 1.5% NaOH and 10% consistency at 90 psi and 100°C, see Fig. III.6 for remaining conditions).
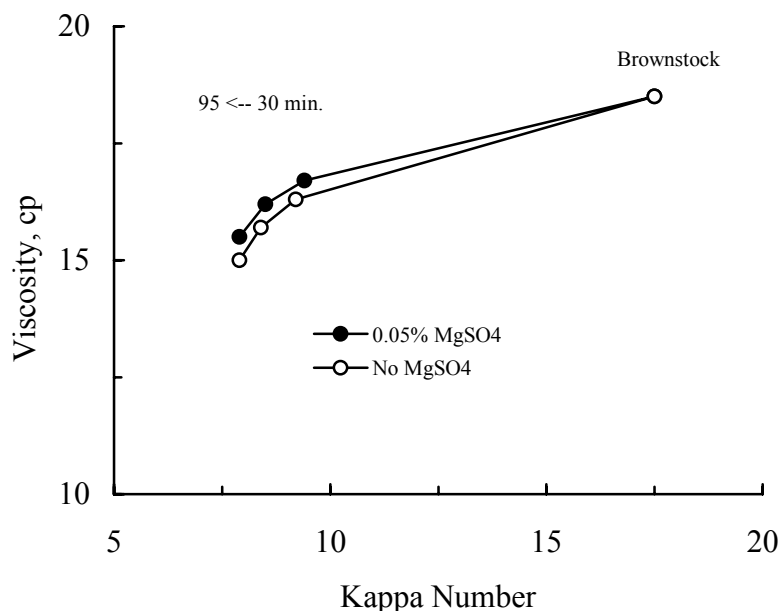
Figure V.8. Influence of added magnesium on delignification selectivity of CHK pulp (Oxygen bleaching with 1.5% NaOH and 10% consistency at 90 psi and 100°C, see Fig. V.6 for remaining conditions).

Effect of Changing the Magnesium Levels on O-Delignification Selectivity

To study the influence of magnesium levels on oxygen delignification selectivity, the metal ions in HKA were removed by an acid washing procedure. As shown in Table V.3, the washing removed most of Mn and Mg ions from the pulp.

Table V.3. Metal ions content (ppm) of aspen kraft pulp before and after acid washing.

Sample	Mn	Fe	Cu	Co	Mg	Ca
HKA	10.1	5.4	19.4	trace	230	4090
Acid Washing	1.2	4.8	6.9	trace	34.5	414

Figure III.9 illustrates the selectivity of the oxygen delignification as related to the concentration of magnesium sulfate. The results clearly demonstrates that the selectivity of O-delignification increases significantly when low amounts of magnesium are added to the pulp followed by a slow increase after the magnesium concentration reached 400 ppm. Interestingly, Brown[21] suggested that if pulp contains approximately 1000 ppm magnesium, it is unnecessary to add further amounts of magnesium sulfate. The lower levels of magnesium required in this study are probably due to the low content of deleterious metal ions in the pulp after acid washing. Although the selectivity shown in Figure V.9 still increases even after 2000-ppm magnesium, the lignin removal becomes very slow. A similar phenomenon was reported by Jarrehult and Samuelson.[22]
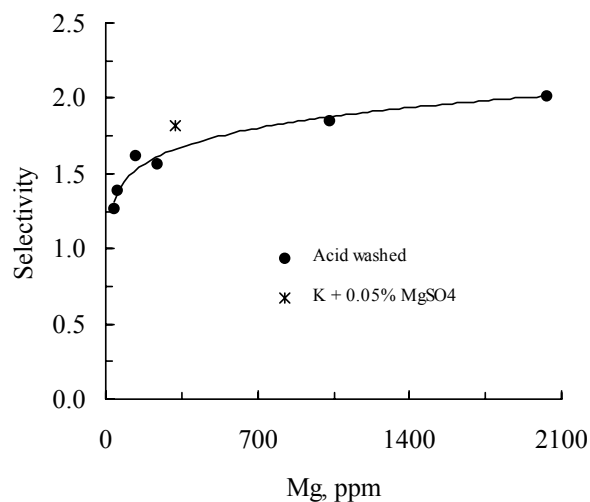
Figure V.9. Influence of magnesium concentration on oxygen delignification selectivity (Oxygen bleaching with 1.5% NaOH and 10% consistency at 90 psi and 100°C for 1 hr.).

Figure V.9 also indicates that the addition of magnesium sulfate to the kraft pulp without acid washing led to a slightly higher delignification selectivity in spite of the higher content of transition metal ions content. This observation may be due to the "native magnesium" being more effective than the added portion.[23]

Effect of Mixing Speed on Oxygen Delignification

As discussed previously, pulp mixing is another important component to overall efficiency of O-delignification of kraft pulps. To further explore the role of mixing in oxygen delignification another softwood kraft pulp (SKP) was O-delignified under varying mixing conditions, as summarized in Table V.4.

As indicated, kappa number reduction increases substantially with mixing in the low-speed range. This trend is more clearly indicated in Figure V.10. Comparing the delignification without agitation, interval mixing at 300 rpm resulted in 7% more lignin removal. A further increase in mixing speed from 300 rpm to 600 rpm led to another 2% higher lignin removal. However, as mixing speed reached approximately 1000 rpm, the effect of mixing on oxygen delignification leveled off. The results are generally in agreement with the studies conducted by Yaldez and Stark,[6] whose results indicated that the increase in oxygen delignification correlated with an increase in mixing speed up to 850 rpm. The presence of a maximum mixing speed is rationalized in terms of mass transfer. As discussed by Reeve and Earl,[9] under fluidized conditions, the pulp suspension behaves similarly to water. In this state, mass transfer should reach a maximum. Yaldez and Stark[6] proposed that optimal mixing occurs just above the point of fluidization. According to Gullichsen and Harkonen,[24] the mixing speed for

fluidization of a pulp suspension is a function of pulp consistency, torque, and the geometry of the reactor and rotor.

Table V.4. The influence of mixing speed on oxygen delignification[a] of the softwood kraft pulp.

Sample	Speed, rpm	Kappa Number	Freeness CSF	Viscosity cp
1		30.4	750	35.2
2	0	15.7	750	21.4
3	300	13.6	750	21.7
4	600	13.0	750	20.8
5	1200	12.5	730	21.2
6	1800	12.3	710	21.6
7	2500	12.6	675	21.8
8	600	12.8	-	-
9	600	13.3	-	-

Mixing time 5 seconds every two minutes.
a: NaOH 2.5%, $MgSO_4$ 0.1%, 100 ºC, 90 psi, 10% consistency for 1 hr.
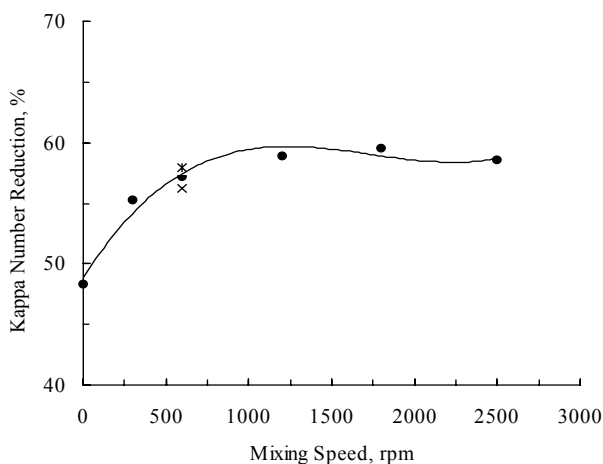
Figure V.10. Influence of mixing speed on kappa number reduction after oxygen delignification. (NaOH 2.5%, $MgSO_4$ 0.1%, 100 ºC, 90 psi, 10% consistency for 1 hr.)

Hence although these results limited to the reactor employed in this study, it does suggest that mixing speed could impact the oxygen delignification. Therefore, it is expected that the different types of reactor available may have different mixing speeds for optimal oxygen delignification. In the CRS reactor used, the optimal mixing speed appeared to be 1000 rpm.

Changes in the time of mixing do not appear to create significant differences. This

observation is inconsistent with what has been reported by Iijima and Taneda.[7] Their results indicated that a reduction of mixing time from 10 seconds to 5 seconds caused a substantial decrease in lignin removal. The discrepancy is probably due to the differences in experimental design and protocol. In the study conducted by Iijima and Taneda,[7] mixing was only applied at the beginning, whereas in this study an interval mixing throughout the whole process was used.

Effect of Mixing Speed on the Physical Characteristics of Oxygen-Delignified Pulps

Because of the considerable energy input, pulp beating is likely to occur at high speed mixing. As indicated in Figure V.11, pulp freeness decreases significantly after surpassing a mixing speed of 1200 rpm. This result is in agreement with what has been reported by Reeve and Earl[9] and what has been predicted by Gullichsen and Harkonen.[24] Interestingly, Yaldez and Stark[6] reported that no pulp-beating effect was observed even when the mixing speed was ramped to 3220 rpm. The different observation may be attributed to the reactor geometry. In our studies a medium consistency reactor was employed that has two smooth ribs located opposite each other in the reaction chamber enhance pulp mixing. No such ribs were present in the reactor used by Yaldez and Stark.[6]
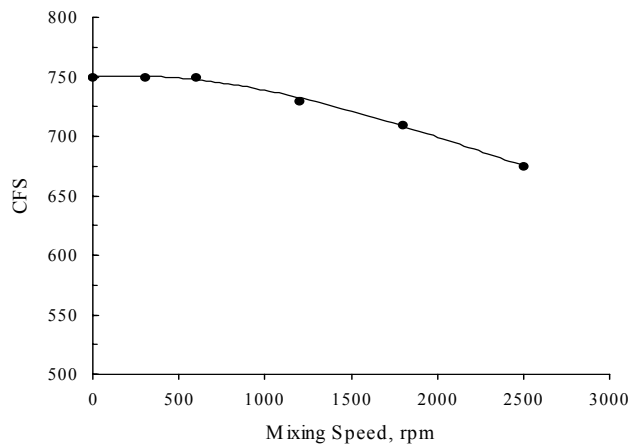
Figure V.11. Influence of mixing speed on pulp freeness after oxygen delignification of softwood kraft pulp.

The study was further extended to investigate the effect of mixing intensity on pulp viscosity. As shown in Figure V.12, oxygen delignification resulted in a 40% viscosity reduction.
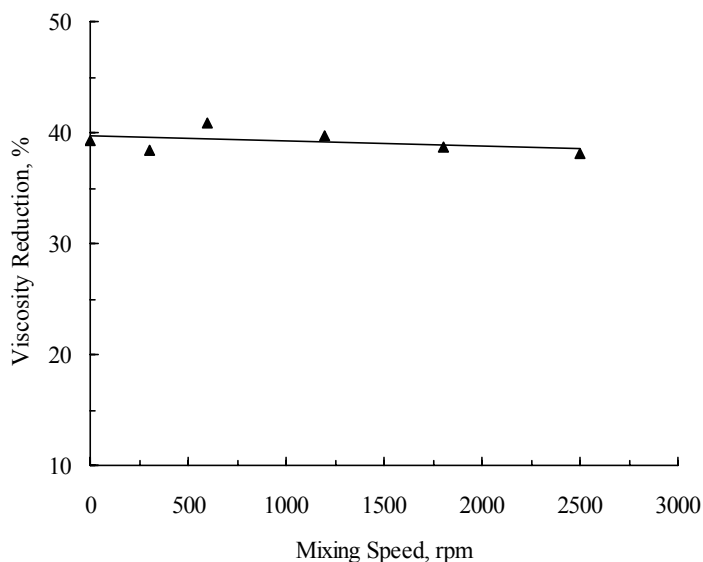
Figure III.12. Viscosity reduction after oxygen delignification of softwood kraft at different mixing speeds (NaOH 2.5%, MgSO$_4$ 0.1%, 100 ºC, 90 psi, 10% consistency for 1 hr.).

However, no significant difference in pulp viscosity was observed due to the speeds (0 to 2500 rpm). This indicates that mixing at high speed increased the specific surface of the fiber, whereas the damage to the fibers was negligible.

Chapter V: Experimental

Materials and Reagents: Two southern pine kraft pulps (SK and SKP) with initial kappa number of 29.7 and 30.4 respectively were acquired from the mills in the state of Georgia. The two hardwood kraft samples, HK, HKA, were acquired from an industrial source and were produced from sweet gum, whereas the other hardwood pulp, CHK, was obtained from a pulp mill in the state of Georgia and was produced from mixed hardwood species. All the chemicals used were commercially purchased and used as received.

Oxygen Delignification: Delignification was conducted in either a CRS (CMS 2040 High Intensity Mixer) or pressurized reactor with continuous mixing. The CRS was specially built by Omega Engineering, Inc. to conduct delignification under pressure (20-30 bar) and high speed (up to 3000 rpm). The pulp with proper amounts of water and magnesium sulfate (if it was applied) was heated to 90°C, and caustic was added as a 1N solution.

Pulp Chelation: Chelation treatment of the pulps followed the procedure described by Bouchard.[25] In general, the pulp was brought to about 3% consistency with 50°C water and the pH of the slurry was adjusted to 5.5 with 4N sulfuric acid. The treatment

continued for 30 min and then the pulp was completely washed with deionized water. The washed pulp was centrifuged and stored in a cold room (< 3°C) for later use.

Acid Washing.　　The treatment followed the similar procedure employed by Bouchard et al.[25] A plastic container filled with 10 L water (pH 1.5) was placed in a water bath (70°C). After the temperature reached equilibrium, proper amounts of pulp were mixed into the bucket so that the final consistency was about 3%. The treatment continued for 30 minutes, followed by complete washing with deionized water. The centrifuged pulp was stored in a cool room until used.

Pulp Analysis.　　Pulp kappa number was measured by following micro kappa number procedure (UM246), whereas the measurement of pulp viscosity followed the Tappi standard procedure (T230 OM-82). Metal ions were analyzed by a Perkin Elmer Optima 3000 DV ICP Emission Spectrometer.

Chapter V. Conclusions

This study has focused on the effect of two parameters that have significance for most kraft-oxygen mills: mixing speed and metals management. The interaction between magnesium and metal ions is likely responsible for the improvement of oxygen delignification selectivity. Yet, addition of magnesium leads to a decrease in delignification but an increase in pulp viscosity. The retarded delignification may be attributed to the reduction in radical formation and/or the decrease in alkalinity of the bleaching system. It was also found that the extent to which the delignification selectivity can be improved by the addition of magnesium closely correlates to the magnesium content in the pulp. High magnesium content in the pulp causes the addition of magnesium sulfate to be less important during oxygen delignification.

The effect of mixing speed on oxygen delignification of softwood kraft pulp was important and was found to reach an optimum at approximately 1000 rpm. It also led to a decrease in CFS freeness, but no difference in viscosity was observed at various mixing speeds.

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Chapter VI. Oxygen Delignification of SW Kraft Pulp and Resulting Pulp Properties

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. 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 others[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] Argyropoulos and Liu,[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.

Chapter VI. Experimental

Materials. 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 (100g 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 (50g 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 x 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, 90º pulse angle, 14-s pulse delay, 23,000-Hz sweep, 11-40,000 transients, at 50.0ºC. 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, 90º 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.

Chapter VI. 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 V.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. 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.

Table VI.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

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 analyzed using advanced NMR techniques. Table VI.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 Figure VI.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 VI.2.

Table VI.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-Hydroxy-phenyl 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

Interestingly, the spectral data in Figure VI.2 indicate that a peak at δ191 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 δ191 indicated that the intensity of this peak increased by 53% for the SW1-2 residual lignin with respect to SW1-O.
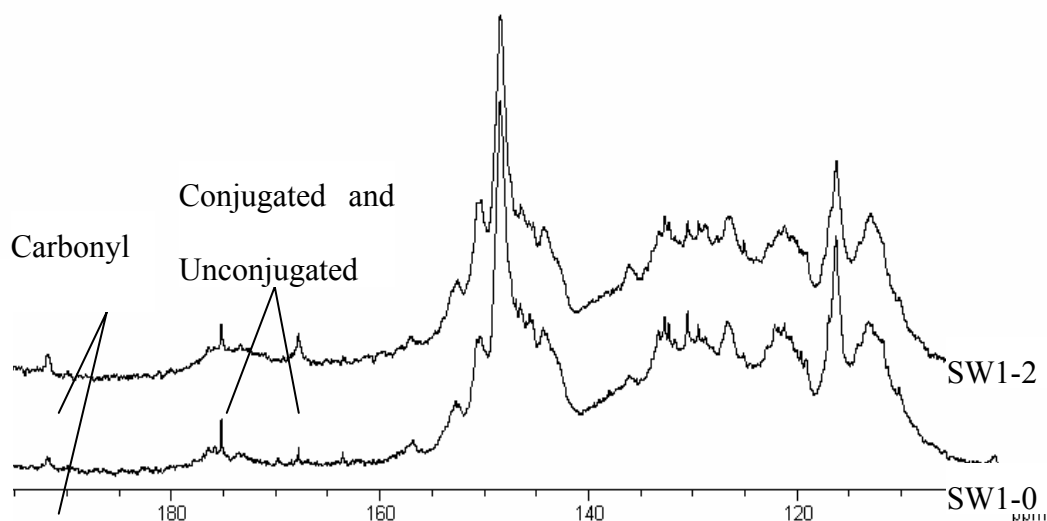
Figure VI.2. ^{13}C NMR spectra (40,000 Scans) of isolated lignin from brownstock SW1-0 and oxygen delignified kraft SW1-2.

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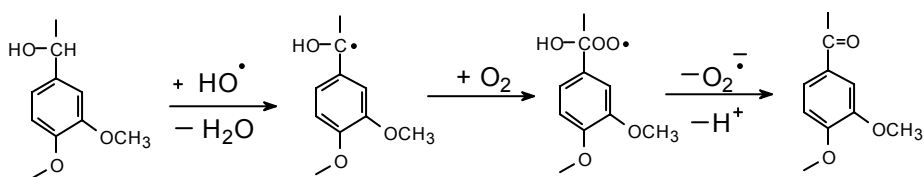
Figure VI.3. The formation of α-carbonyl group in lignin during the oxygen delignification.[10]

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

Table VI.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.

Conjugated Carboxyl acid
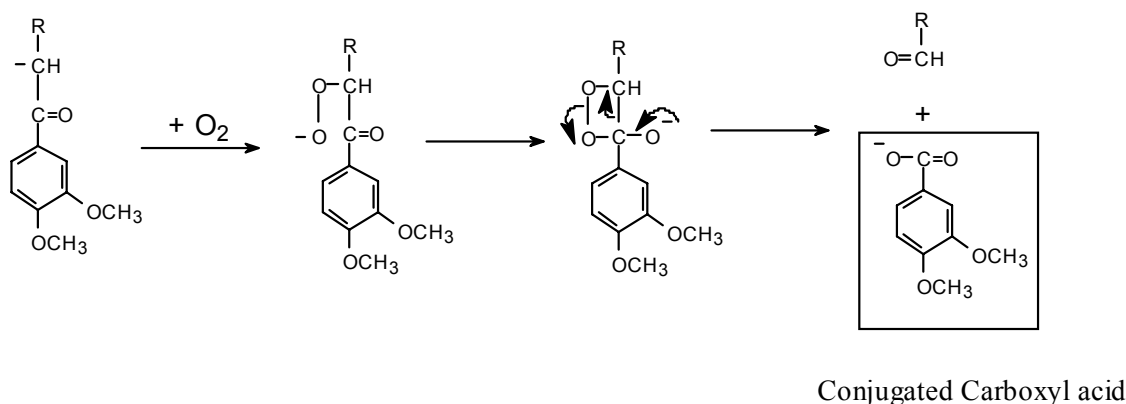
Figure VI.4. Formation of conjugated carboxyl acid through side chain cleavage.

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

^{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.

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 VI.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 VI.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	9.20	2.69	0.118±0.005	1.27
SW1-2	7.40	2.73	0.114±0.005	1.30
SW1-3	6.90	2.70	0.108±0.005	1.24
SW2-0	6.56	2.80	0.082±0.004	0.97
SW2-1	6.60	2.74	0.120±0.005	1.26
SW2-2	5.70	2.72	0.102±0.004	1.17
SW2-3	5.80	2.81	0.111±0.005	1.21

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

Table VI.5. Physical strength of brownstock and oxygen delignified kraft pulps.

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

[1]see Table VI.1 for oxygen delignification conditions.

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]

Chapter VI. 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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VII. Oxygen Degradation Hardwood Kraft Pulps

The bleaching of HW kraft pulps is an integral component in the overall production of high-value pulp fibers.[1] Over the last two decades these operations have faced a series of new environmental regulations.[2] As a result, oxygen delignification has become a strategic technology employed to remove residual lignin from HW kraft pulps and improve the overall environmental performance of bleach plant operations. Although the chemistry of SW kraft pulp oxygen delignification[4-6] has been extensively studied, few studies have been directed towards HW kraft pulps.[7,8]

The natural abundance of syringyl phenylpropanoid moieties in HW furnishes is known to dramatically influence the overall pulping and bleaching reactivity of this wood source. The linkage and the relative content between syringyl and guaiacyl units in hardwood lignin have been a topic of intensive study.[10,11] It is generally accepted that guaiacyl and syringyl units are discretely copolymerized in various ratios depending on different species and different morphological regions.[12] Studies by Yokoi et al.[13] have reported syringyl/guaiacyl ratios varying from 1.00:1.57 to 1.00:2.13 in a radial distribution from the pith for Eucalyptus camaldulensis. NMR studies by Manders et al.[14] have reported syringyl/guaiacyl ratios of 1:1 for birch and 0.85:1.00 for maple based on ^{13}C CPMAS NMR data. Martinez et al. reported ratios of 1.00:1.94 to 1.00:3.95 for a series of Austral hardwoods.[15]

Interest in syringyl:guaiacyl ratios are due, in part, to the well-known beneficial effects of syringyl units in HW furnishes for kraft pulping operations. Kondo et al.[16] reported that the cleavage of syringyl-type -O-4 linkage units proceeded twice as fast as analogous guaiacyl units under typical kraft and soda cooking conditions. This result is in good agreement with the practices of hardwood pulping as it has been clearly demonstrated that delignification in hardwood kraft pulping proceeds more quickly than the pulping of softwood species.[17] At the completion of kraft pulping HW furnishes, the syringyl:guaiacyl ratio has been altered and is typically enriched with guaiacyl units.[18,19]

In spite of the high reactivity of hardwood lignin towards alkaline pulping, several investigators have reported that HW kraft pulps are less responsive to oxygen delignification conditions than SW kraft pulps. For example, Chirat and Lachenal[20] reported that a four-stage oxygen delignification sequence was more effective at removing lignin from a SW kraft pulp than a HW kraft pulp. Similarly, Sun and Argyropoulos[21] have reported that softwood kraft pulps were more readily oxygen delignified than hardwood kraft pulps. Although no mechanism was proposed to account for the low reactivity of hardwood kraft pulp lignin toward oxygen delignification, it has generally been attributed, in part, to the structural components present in the lignin. Further advances in oxygen delignification of HW kraft pulp are dependent upon an increased understanding of the chemistry involved in this process.

In this study, a series of sweet gum kraft pulps, prepared from a modified batch and conventional kraft batch pulping procedure, were subjected to oxygen delignification under varying charges of alkali. The lignin chemistry of oxygen delignification was

evaluated by isolating and characterizing lignin from the kraft brownstocks, post-oxygen delignified counterparts, and O-bleached effluents. The changes in lignin structure due to the oxygen stage were then attributed to the chemistry of oxygen delignification.

Chapter VII. 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. Filtered Nanopure™ deionized (DI) water was used in all instances when water was required.

Wood Source and Chip Processing. The chips used for the pulping experiments were obtained from a fresh sweet gum tree that was cut in south Georgia, U.S.A. The wood was debarked, split, and chipped. The chips were then mixed and screened. The chips were screened by first collecting the fraction that passed though a 6-mm bar screen. The accepts were then screened on a ¼" mesh screen to remove all the small debris.

Kraft pulps. Three sweet gum Rapid Displacement Heating (RDH) kraft pulps[22] (K29, K23, and K14 with kappa numbers 29.0, 22.9, and 13.6 respectively) were prepared using a fully automated control system employing 4:1 liquor/wood ratio, 30% sulfidity (active alkali basis), and 165°C maximum cooking temperature.[23] White liquor addition was split into warm and hot black liquor pretreatments. The wood chips were pretreated with warm and hot black liquors before cooking with white liquor. At the end of the cook, hot cooking liquor inside the digester was displaced back to the hot and the warm black liquor accumulators using washer filtrate from a brownstock washing system. The active alkali charge and cooking H-factor were varied from 11.2 to 13.8 and 200 to 300, respectively, so that different kappa pulps were obtained. A conventional kraft pulp (KC14, kappa number 14.4) was prepared at a 4:1 liquor/wood ratio, 13.6% AA (as Na_2O), and 30% sulfidity (active alkali basis). Sweet gum chips and cooking liquor were heated to 165°C for 90 minutes and kept at that temperature until 1,100 H-factor was reached.

Oxygen Delignification. A 2-L reactor equipped with a continuous mixing device was used for all oxygen delignification experiments. In a typical experiment, the reactor was warmed to 70°C, charged with pulp (80g dry weight), $MgSO_4$ solution (0.05% wt/wt basis), the desired amount of 1.00 N NaOH solution, and deionized water so that the final pulp consistency of 10% was reached. The reactor was then sealed, pressurized with O_2 (90 psi) and rapidly heated to 100°C with mixing. The reaction was allowed to proceed for one hour with stirring, after which the pulp and effluents were collected.

Hexenuronic Acid Analysis. The content of hexenuronic acids in the HW kraft pulps was assessed indirectly by refluxing the pulp samples in a formic acid-sodium formate buffer as described in the literature.[24]

Pulp Characterization. The lignin content of the kraft pulps in this study was determined by a $KMnO_4$ titration of the pulp in accordance with TAPPI Standard Methods T236-cm85. The viscosity of the pulp was measured employing a capillary

viscometer as described in TAPPI method T-230.[25]

Lignin Isolation and Purification. Residual lignin was isolated from the kraft pulps employing a mild acid hydrolysis procedure that has been described in the literature.[26] Dissolved lignin in the O-effluents were isolated by acid precipitation (pH 2.5) and subsequently washed with 1.00 N HCl (2 x 250 mL). The aqueous supernatant was further extracted with diethyl ether (3 x 250 mL). The acid-precipitated lignin and solvent-extracted lignin were combined and purified by Soxhlet pentane extraction.

Differential UV/Vis Analysis of Residual Lignin. A Lambda 900 UV spectrometer was employed for the differential UV spectroscopy studies of isolated lignin, following the procedure described by Pasco and Suckling.[27]

^{13}C and ^{31}P NMR Analysis of Residual Lignin. The isolated lignin samples were analyzed using a 400 MHz Bruker DMX spectrometer. Quantitative ^{13}C NMR spectra were acquired and analyzed in accordance with established literature methods.[28] ^{13}C NMR spectra were recorded with an inverse gated decoupling sequence, 90º pulse angle, 14-s pulse delay, 23,000-Hz sweep, 10-12,000 transients, at 50.0ºC. The Fourier transformed spectra were integrated according to reported chemical shifts for lignin functional groups. The integrals were normalized to the aromatic signals, which were assumed to have a value of 6 carbons.

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.[29-31] ^{31}P NMR spectra were recorded using an inverse gated decoupling sequence, 90º pulse angle, 25-s pulse delay, 13,000-Hz sweep, and 300 transients, at room temperature. Table VII.1 summarizes the standard deviation associated with the ^{13}C and ^{31}P NMR measurements.

Table VII.1. ^{13}C and ^{31}P NMR Experimental Error Analysis for Lignin Samples

Functional Group	Standard Deviation[a]	Functional Group	Standard Deviation[a]
^{13}C NMR Unconjugated COOH	4.6×10^{-2}	^{31}P NMR Aliphatic hydroxyl	3.0×10^{-2}
Conjugated COOH	2.1×10^{-2}	Syringyl phenolics	7.6×10^{-3}
Substituted aromatic	2.7×10^{-2}	C5 condensed guaiacyl	7.6×10^{-3}
C6 in guaiacyl	7.5×10^{-3}	C5 uncondensed guaiacyl	5.8×10^{-3}
C5 in guaiacyl	9.4×10^{-3}	Catechol phenolics	1.3×10^{-2}
C2 in guaiacyl	2.4×10^{-2}	Carboxylic acids	2.4×10^{-2}
C2 and C6 syringyl	1.7×10^{-2}		
Methoxyl Carbons	3.1×10^{-2}		

[a]Standard deviation was calculated based on three (^{31}P) or four (^{13}C) independent NMR experiments.

Chapter VII. Results and Discussion

Oxygen delignification of modified and conventional sweet gum kraft pulp. The chemistry of oxygen delignification was explored employing a series of RDH and conventional kraft pulps with varying lignin content. These pulps were subjected to a conventional oxygen delignification stage using a low (1.00%) and high (4.00%) charge of sodium hydroxide, as summarized in Table VII.2.

Table VII.2. Physical properties of kraft SW brownstocks and oxygen delignified pulps

Samples[a]		K29	K23	K14	KC14
Brownstock	Kappa	29.0	22.9	13.6	14.4
	Viscosity, cP	27.8	28.0	24.8	23.3
O-delignified 1% NaOH	Kappa number	22.4	15.8	8.3	9.3
	Kappa Reduction, %	22.8	31.0	39.6	35.4
	O-Bleachability[b]	6.6	7.1	5.3	5.1
	Viscosity, cP	20.3	19.7	16.8	15.6
	Viscosity reduction, %	26.8	29.6	32.2	31.1
	Yield, %	98.5	98.0	98.7	98.2
O-delignified 4% NaOH	Kappa number	10.8	9.1	7.0	8.1
	Kappa Reduction, %	62.8	60.3	48.5	43.8
	O-Bleachability[2]	4.6	3.4	1.6	1.6
	Viscosity, cP	15.0	15.0	12.1	11.5
	Viscosity reduction, %	46.0	46.4	51.2	52.0
	Yield, %	96.7	96.9	97.6	96.8

[a]initial brownstock kraft pulps; [b]oxygen bleachability was calculated as Δkappa/NaOH charge.

Oxygen bleachability of the pulps was shown to be dependent on the charge of sodium hydroxide and the incoming kappa number of the brownstock pulp, whereas no differences in O-bleachability were observed between the low kappa modified and conventional batch kraft pulps. The results in Table VII.2 also indicate that O-bleachability decreases as the charge of caustic is increased. These results are consistent with our previous report that softwood kraft pulps frequently contain a certain amount of lignin that is readily removed under oxygen delignification and another component that is difficult to remove.[32] Furthermore, the reactivity of HW kraft pulps towards an O-stage is diminished as the incoming pulp kappa number is reduced. It is also apparent that the pulp carbohydrates were significantly degraded when the higher alkaline charge was employed, as the pulp viscosity and yield decreased.

Based on prior literature results, the observed oxygen bleachability results could be influenced by the structural nature of lignin and 4-deoxy-β-L-threo-hex-4-enopyranosyluronic acid (hexenuronic acid) present in the pulp.[24] Hexenuronic acids are formed during kraft pulping from base-catalyzed elimination of methanol from 4-O-methyl-glucuronic acids. These unsaturated carbohydrates contribute to the kappa number of kraft pulps and consume electrophilic bleaching agents such as chlorine

dioxide and ozone and are resistant to nucleophilic bleaching including alkaline peroxide and oxygen. The percent contribution of hexenuronic acids to the pulp kappa number of K29, K23, K14, and KC14 was determined following literature methods and found to be 9, 13, 40, and 51%, respectively. After oxygen delignification, the hexenuronic acid contribution to the post- O-delignification HW kraft pulp was found to remain the same or increase slightly. These results are consistent with past reports suggesting that hexenuronic acids are resistant to an O-stage. In light of the known resistance of hexenuronic acids towards O-delignification and the relative high contribution of these sugars towards the pulp kappa number of K14 and KC14, the reduced bleachability of these two pulps can be attributed, in part, to the significant concentration of hexenuronic acids in these pulps.

To explore the involvement of residual lignin in influencing the O-bleachability of the HW kraft pulps, lignin samples were isolated and spectroscopically analyzed from the brownstock and post-oxygen delignified pulps. Table VII.3 summarizes the yield of isolated lignins from the kraft pulps and O-effluents. In general, the yield of residual lignin from the post-oxygen delignified pulps decreased as the degree of O-delignification increased. This effect was attributed to the oxygen delignification process introducing additional acid groups into the lignin that in turn increased the water solubility of lignin and thus resulted in reduced lignin recovered during the lignin isolation process.

Table VII.3. The yield of lignin isolated from pulps and effluents

Starting Pulp	Description of Lignin Sample	Brownstock		O-Stage 1% NaOH		O-Stage 4% NaOH	
		Lignin	Yield[a]	Lignin	Yield	Lignin	Yield[b]
K29	Residual lignin from pulp	R29	67.8	R29O1	49.8	R29O1	51.3
	O-effluent oxidized lignin			R29E1	38.5	R29E1	41.5
K23	Residual lignin from pulp	R23	65.7	R23O1	56.8	R23O1	43.3
	O-effluent oxidized lignin			R23E1	41.6	R23E1	39.4
K14	Residual lignin from pulp	R14	56.5	R14O1	48.3	R14O1	31.7
	O-effluent oxidized lignin			R14E1	41.7	R14E1	42.2
KC14	Residual lignin from pulp	C14	64.6	C14O1	47.9	C14O1	30.5
	O-effluent oxidized lignin			C14E1	38.3	C14E1	43.2

[a]Residual lignin yield was calculated by: [mass of lignin isolated/(initial kappa number of brown stock x 0.15 x mass of pulp)] after taking into account hexenuronic acids contribution. [b]Lignin yields from O-effluents were determined by: (mass of lignin recovered)/[(kappa decrease during O-stage x 0.15 x mass of pulp employed)].

Differential UV/Vis Spectroscopy. The UV/Vis difference spectrum of residual lignin R29 is shown in Figure VII.1. It is generally considered that the UV/Vis absorption properties of etherified lignin units are unchanged in neutral and alkaline medium,[33]

whereas the absorption maximum bands of phenolic moieties shift to longer wavelengths at high pH due to the ionization of phenolic hydroxyl group. Hence, the difference UV/Vis spectra recorded in neutral and alkaline pH range provide a convenient means of evaluating the phenolic hydroxyl content of lignin.
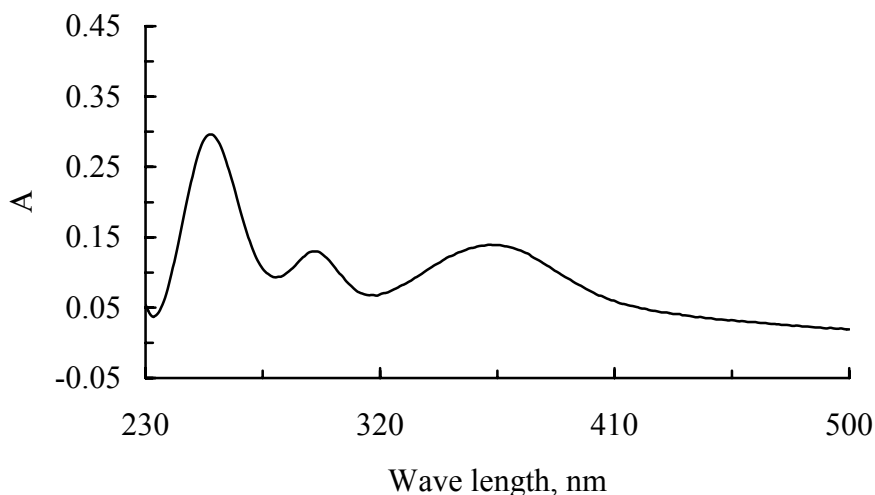
Figure VII.1. UV/Vis difference spectrum of lignin isolated from R29.

The three absorption peaks in Figure VII.1 at λ_{max} 260, 280, and 370 nm are attributed to phenolic lignin structures. Based on lignin model compound studies by Aulin-Erdman,[34] the peaks at λ_{max} 260 and 280 nm can be attributed to ionized nonconjugated phenolic lignin units. The peak centered at around λ_{max} 370 nm has been attributed to conjugated phenolic units such as stilbene-type structure **2** in Figure VII.2.[35]
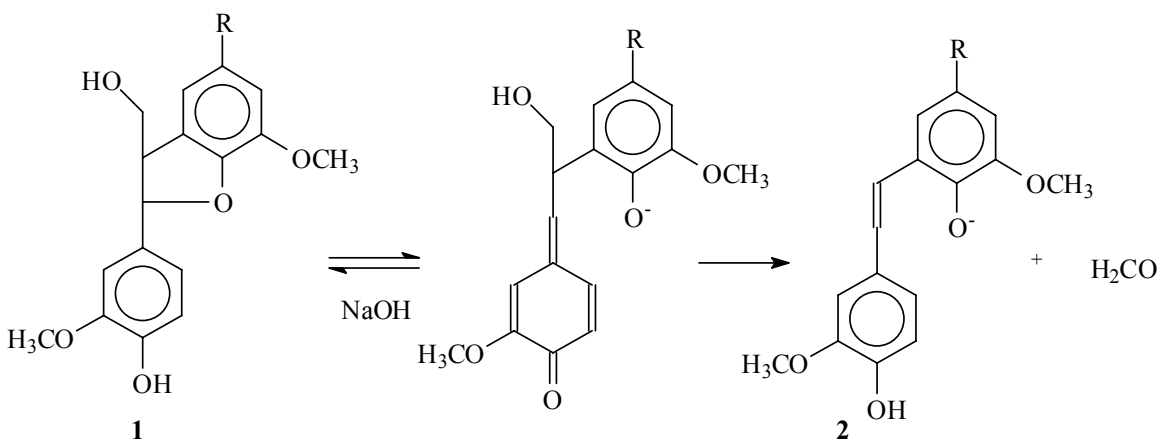
Figure VII.2. Formation of stilbene-type structures during alkaline pulping.

The formation of stilbene-type structures in kraft pulps is well known and is generally attributed to the degradation of phenylcoumaran **1** during alkaline pulping, as indicated in Figure VII.2.[36] Although the presence of hydrosulfide ion in kraft cooking liquor can

depress the formation of these stilbene-type structures, once these moieties are generated they are stable under alkaline pulping conditions and accumulate in the pulp.[37]   The results presented in Figure VII.1 are consistent with these results as the differential UV/Vis analysis indicated substantial amounts of phenolic stilbene units in residual lignin of the kraft brownstocks.

Figure VII.3 summarizes the UV/Vis difference lignin spectra data acquired from kraft brownstock R29, post-oxygen delignified R29O4, and O-effluent lignin R29E4.   The nonconjugated phenolic lignin signals at λ_{max} 260 and 280 nm were clearly decreased for the lignin samples isolated from the oxygen delignified pulp and the O-effluent lignin. Similarly, sample R29O4 had diminished signal intensity at λ_{max} 370 nm indicative of reduced stilbene-type structures in the oxygen delignified residual lignin.   The UV/Vis difference spectrum of R29E4 had an absorption at λ_{max} 370 nm suggesting the presence of phenolic stilbene-like structures. However, based on the known reactivity of stilbene-type structures in alkaline oxygen medium[38] it seems unlikely these structures could survive an oxygen stage. Hence, it is uncertain at this stage what structure(s) in dissolved O-effluent lignin contribute to this absorption.

1.1
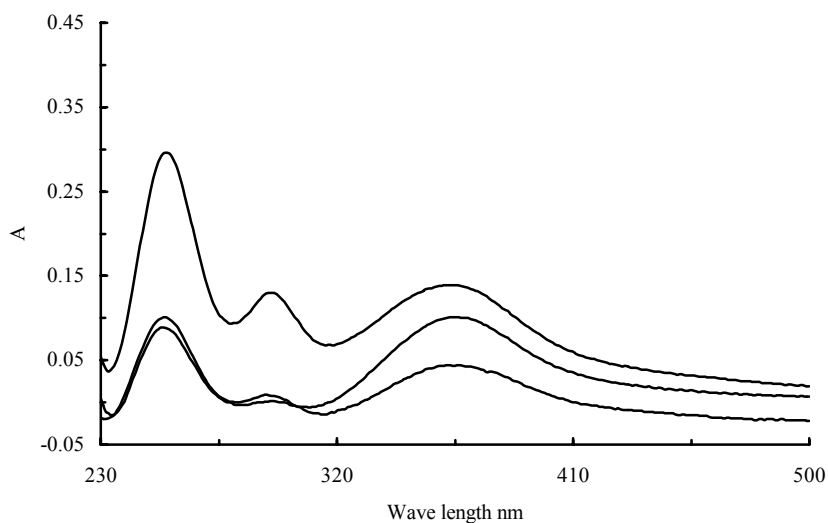
Figure VII.3. Differential UV/Vis spectra of lignins isolated from kraft R29, oxygen delignified R29O4, and oxygen bleaching effluent R29E4.

NMR Lignin Studies.   The structural changes occurring to lignin during O-delignification were further analyzed by phosphyliting the lignin samples and employing ^{31}P NMR to quantitify the amounts of syringyl, guaiacyl, C-5 condensed phenolics, aliphatic hydroxyl, and carboxylic acid groups in the lignin samples. The results of this analysis are summarized in Table VII.4 and Figures VII.4 to 7.

Table VII.4. ^{31}P NMR analysis of phosphitylated residual lignin samples[a] from kraft brownstocks. post-oxygen delignified pulps and O-effluent lignins.

| Sample[b]	Aliphatic Condensed	C5 Guaiacyl	Syringyl	C5 Noncondensed Guaiacyl	Catechol	Carboxyl
<u>R14</u>	2.25	0.34	0.61	0.32	0.13	0.43
R14O1	2.38	0.35	0.51	0.13	0.08	0.74
R14O4	2.45	0.38	0.42	0.12	0.08	1.08
R23	2.40	0.36	0.63	0.29	0.13	0.32
R23O1	2.79	0.34	0.52	0.24	0.13	0.47
R23O4	2.82	0.34	0.35	0.21	0.11	0.72
R29	2.69	0.39	0.72	0.34	0.16	0.27
R29O1	2.61	0.39	0.54	0.22	0.12	0.39
R29O4	2.67	0.31	0.44	0.20	0.14	0.68
C14	1.42	0.53	0.62	0.33	0.21	0.58
C14O1	1.67	0.45	0.49	0.29	0.20	0.98
C14O4	1.53	0.33	0.33	0.18	0.14	1.18
R23E1	2.74	0.19	0.19	0.10	0.07	0.68
R23E4	3.17	0.19	0.18	0.11	0.09	0.79
R14E1	2.13	0.12	0.20	0.10	0.08	0.57
R14E4	2.55	0.16	0.22	0.13	0.10	0.80
C14E1	2.37	0.20	0.15	0.08	0.06	0.65
C14E4	2.29	0.16	0.20	0.15	0.11	0.65

[a]all functional groups were measured as (mmol/gr lignin). [b] see Table 3 for description of lignin codes.

A review of the results in Table VII.4 indicates that the aliphatic hydroxyl group content for residual lignin samples isolated from post O-delignified pulps are enriched with respect to the corresponding kraft brownstock residual lignin samples. This result implies that little side-chain oxidation has occurred to the phenylpropane side chain of residual lignin in post-oxygen delignified pulps. The relative amounts of catechol groups in the pre and post-oxygen delignified pulps also does not vary significantly. This steady state behavior has been noted by Asgari and Argyropoulos for a series of simulated oxygen delignification studies employing kraft lignin.[39] The authors attributed this

behavior to a steady formation of catechols from guaiacol and their subsequent conversion to quinones. A recent report by Zawadzki and Ragauskas[40] has shown that an O-stage can typically increase the concentration of quinones in residual lignin decreased after oxygen delignification. This result could suggest that the conversion of guaiacyl units to quinones is not as efficient or that the quinoidal units undergo further alkaline catalyzed degradation.

Figures VII.4 to 6 summarize the changes in syringyl, C5 condensed, and noncondensed guaiacyl phenoxy groups. The depletion of guaiacyl and syringyl phenoxy units was clearly the most prominent groups to be removed from the post-oxygen delignified kraft residual lignins. (see Fig. VII.4 and 5) In contrast, C5 condensed guaiacyl phenolics were shown to be resistant to oxidation, as evidenced by the very small changes in the concentration of this functional group between brownstock and post-oxygen delignified residual lignins, summarized in Figure VII.6. Accompanying the removal of syringyl and C5 noncondensed guaiacyl phenolic units during oxygen delignification were the generation of new carboxylic acid groups (see Figure VII.7). Both the increase in acid groups and the loss of syrinygl/C5 noncondensed guaiacyl phenolics was proportional to the charge of NaOH employed.
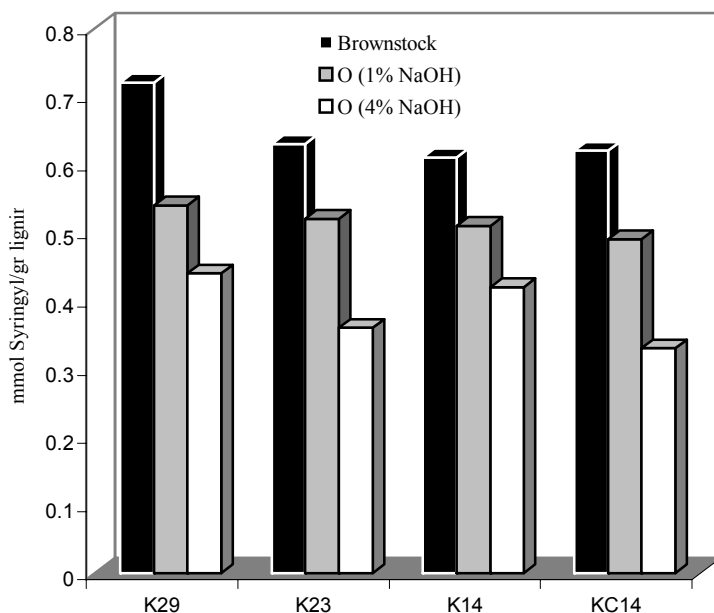
Figure VII.4. Changes in the content of syringyl phenolic units in residual lignin isolated from kraft brownstocks and post-oxygen delignified pulps.
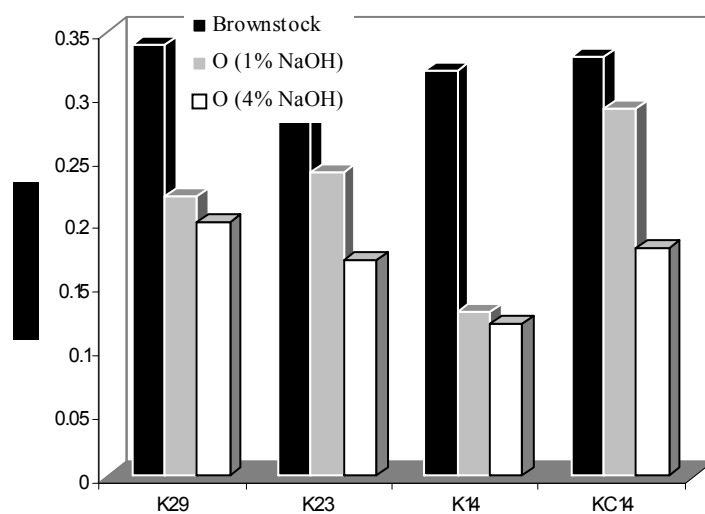
Figure VII.5. Changes in the content of guaiacyl phenolic units in residual lignin isolated from kraft brownstocks and post-oxygen delignified pulps.
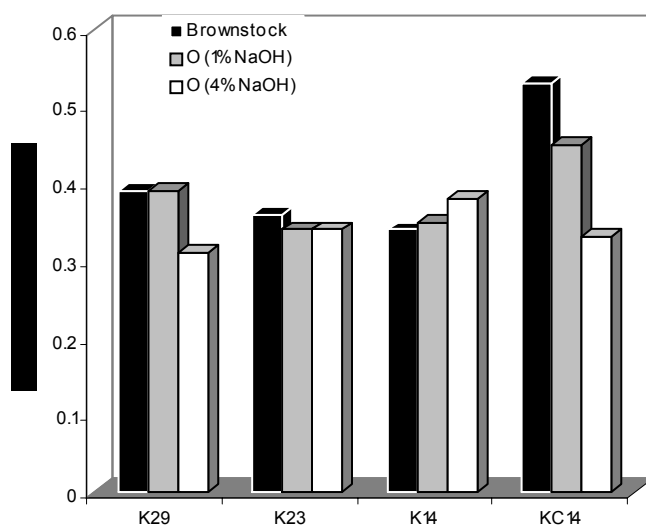
Figure VII.6. Changes in the content of C5 condensed guaiacyl phenolic units in residual lignin isolated from kraft brownstocks and post-oxygen delignified pulps.

Figure VII.7. Changes in the content of carboxylic acid units in residual lignin isolated from kraft brownstocks and post-oxygen delignified pulps.

The increased content of carboxylic groups in lignin samples isolated from oxygen delignified pulps parallels the severity of the O-stage and is undoubtedly a reflection of the increased oxidation of lignin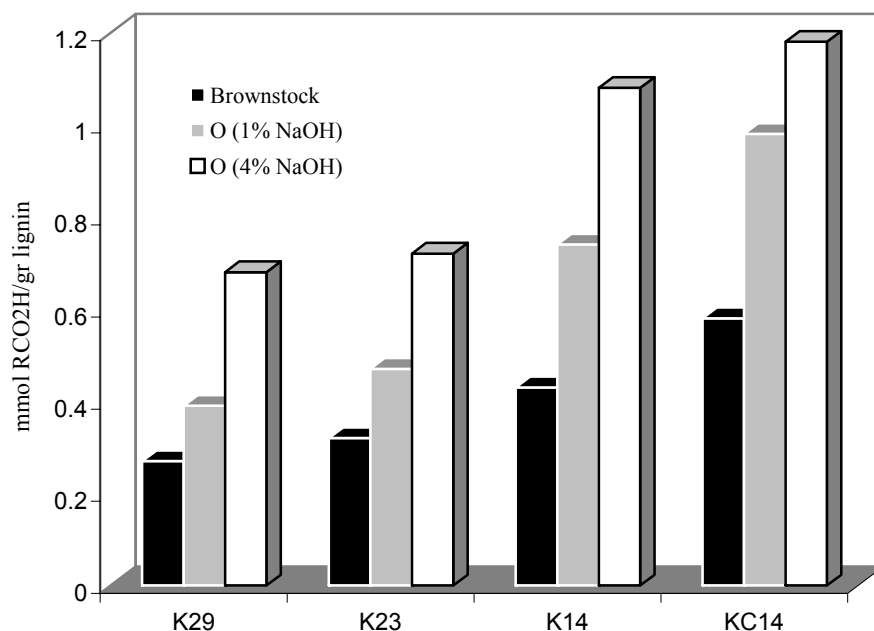 when additional caustic is employed for oxygen delignification.[40] Lignin isolated from the oxygen delignification effluents (see R23E1 and R23E4 in Table VII.3) had a slightly higher carboxylic acid content as compared to the residual lignin in the delignified pulps (R23O1 and R23O4). These results suggest lignin removal during an O-stage is not solely based on improving the solubility of the lignin fragments in an alkaline medium, but instead the oxidative chemistry of O-delignification most likely needs to result in lignin chain cleavage. In this manner, the fragmented lignin components are detached from the macro lignin-cellulose polymer and released into the aqueous effluent.

An inspection of the O-effluent data in Table VII.4 provides additional insight into the overall oxygen delignification process. In general, the O-effluent lignins exhibited a ~10-60% increase in aliphatic hydroxyl groups with respect to the corresponding brownstock residual lignins. These results further support the hypothesis that oxygen delignification does not significantly degrade the phenylpropane side chain of lignin.

The recovered lignin from the O-effluents exhibited >65% decrease in syringyl phenolics and > 55% decrease in C5 noncondensed guaiacyl phenolics with respect to the corresponding values measured for the starting brownstock residual lignins. In contrast to the residual lignin samples, the O-effluent also exhibited significant decreases in the amounts of C5 condensed guaiacyl phenolics although slightly less than the amounts

noted for syringyl and C5 noncondensed phenolics. The acid groups were also shown to increase consistently with the overall oxidative chemistry involved in an O-stage.

^{13}C NMR Lignin Analysis. Although the ^{31}P NMR technique[29] has many advantages for lignin characterization, it can only provide information concerning hydroxyl substituted lignin moieties. Since residual lignin contains a great portion of etherified structures, further characterization of the lignin samples by ^{13}C NMR is necessary.
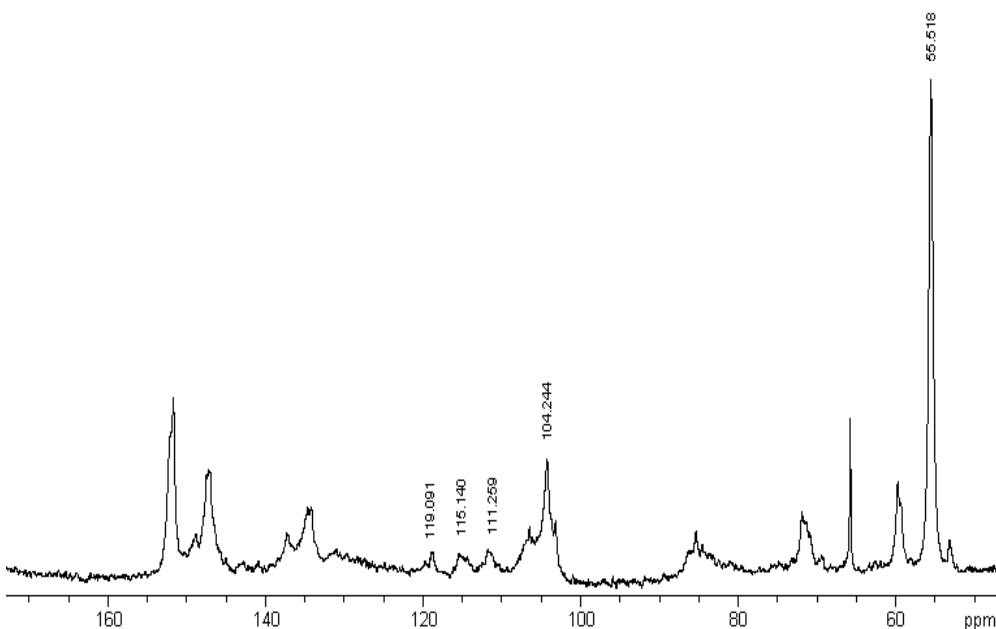
Figure VII.8. ^{13}C NMR spectrum of residual lignin (R29O1) isolated from oxygen delignified K29 with 1% NaOH charge.

A typical ^{13}C spectrum of isolated lignin is shown in Figure VII.8. According to Tai et al.,[41] the peaks centered around 119 ppm, 115 ppm and 111 ppm can be attributed to C_6, C_5, and C_2 carbons in a guaiacyl unit, whereas the signal around 104 ppm was due to C_2 and C_6 carbons in a syringyl unit. The strongest signal at 55.5 ppm was assigned to the methoxyl carbons.

The relative abundance of syringyl and guaiacyl units (including etherified and phenolic) could be determined by the ratio of peak area that corresponded to C_2 and C_6 aromatic carbons in syringyl and guaiacyl units. As such, the total peak area centered at 119 ppm and 111 ppm that corresponded to C_2 and C_6 carbons in a guaiacyl unit was used to divide the area at 104 ppm, which belonged to C_2 and C_6 carbons in a syringyl unit. The ratio was used to estimate the relative content of the two lignin units. Table VII.5 and Figures VII9 and 10 summarize the ^{13}C NMR results of the lignin samples.

Table VII.5. ^{13}C NMR Analysis of Residual Lignin Samples from Kraft Brownstocks. Post-Oxygen Delignified Pulps and O-Effluent Lignins

| Sample	Carboxylic acid	C_2 and C_6 in guaiacyl units	C_2 and C_6 in syringyl units	Ratio of S/G	Methoxyl carbons
R29	0.20	0.69	1.10	1.6	1.39
R29O1	0.24	0.73	1.09	1.5	1.33
R29O4	0.42	0.69	0.93	1.3	1.38
R29E1	0.54	0.65	0.97	1.4	1.33
R29E4	0.87	0.79	0.85	1.1	1.20
R23	0.33	0.74	1.13	1.5	1.36
R23O1	0.49	0.72	1.02	1.4	1.41
R23O4	0.51	0.74	0.99	1.3	1.42
R14	0.44	0.69	0.87	1.3	1.30
R14O1	0.48	0.97	0.95	1.0	1.24
R14O4	0.65	0.85	0.71	0.8	1.24
C14	0.46	0.75	0.81	1.1	1.14
C14O1	0.57	0.86	0.72	0.8	1.19
C14O4	0.73	0.84	0.55	0.7	1.10

It is evident from the results in Table VII.5 that the concentration of carboxylic acids in residual lignin increased with the severity of the oxygen delignification stage, and the changes of these functional groups with the oxygen delignification were in good agreement with the study with ^{31}P NMR analysis stated above.

The methoxy content of the post-oxygen delignified pulps did not statistically differ greatly from the methoxy concentration of starting brownstock residual lignin samples. This result would suggest that the observed steady concentration of catechols (see Table VII.4) present in the lignin before and after oxygen delignification is not due to demethylation of guaiacol units to catechols.
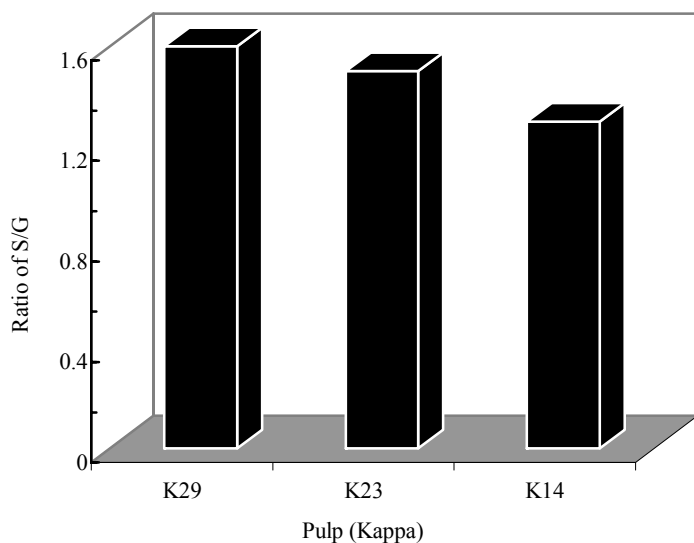
Figure VII.9. A comparison of syringyl to guaiacyl units of residual lignin in brownstock pulps K29, K23, and K14.
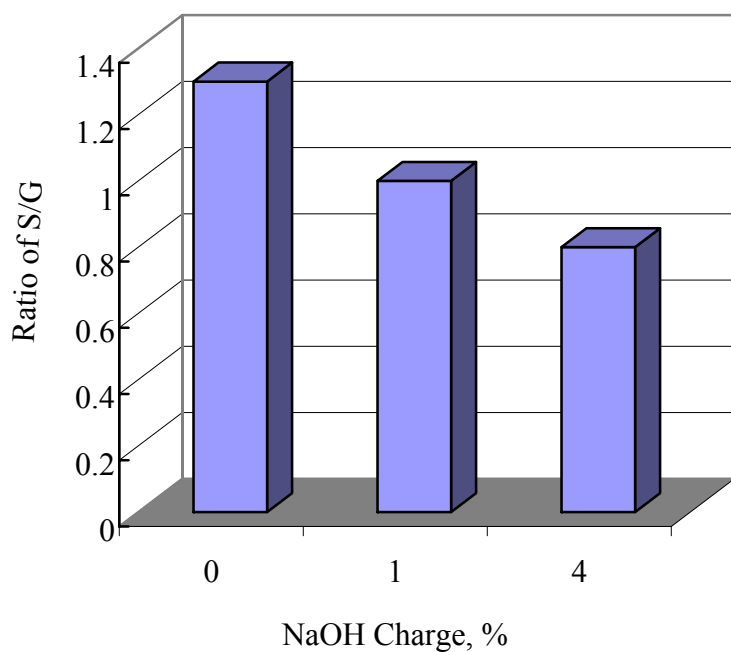
Figure VII.10. A comparison of syringyl to guaiacyl units of residual lignin for different NaOH charges for O-delignification.

The ratio of syringyl to guaiacyl units as determined from ^{13}C NMR data decreased steadily with the removal of lignin during RDH pulping of the sweet gum wood furnish (Figure VII.9). As reviewed in the introduction, model compound studies have shown

that syringyl β-O-aryl ether lignin units are more reactive than the corresponding guaiacyl structures and the data in Figure VII.9 are consistent with these results. The observed difference between K14 and KC14 in syringyl/guaiacyl units was tentatively attributed to differences in pulping technologies.

The ^{13}C NMR analysis also provided a facile method to characterize changes in syringyl/guaiacyl ratios for the post-oxygen delignified pulps, which are summarized in Figure VII.10. Overall it is clear that syringyl units are more reactive to oxygen delignification conditions than guaiacyl lignin units. Studies by Johansson and Ljunggren[42] with lignin model compounds have demonstrated that syringyl model compounds exhibit enhanced reactivity under oxygen delignified conditions, and our results conclusively demonstrate that this result is directly transferable to actual oxygen delignification of HW kraft fibers. The syringyl/guaiacyl trend shown in Figure 9 provides a further confirmation of the high reactivity of syringyl lignin units. As indicated in Figure 10, the syringyl/guaiacyl ratio decreased as the charge of NaOH in the O-stage increased.

Chapter VII. Conclusions

The results reported in this study further define the limitations and opportunities for improvements in oxygen delignification technology. The main functional group contributing to the oxidation of HW kraft residual lignin is syringyl, C5 noncondensed guaiacyl units and stilbene phenolic structures. The inability to oxidize the phenylpropane side chain of lignin and/or C5 condensed guaiacyl phenolics detrimentally impacts O-bleachability. Germer and Shagaev[43] have shown that the introduction of α-carbonyl groups into lignin model compounds can dramatically improve the reactivity of etherified phenolics. The challenge for pulp bleaching research is to develop new oxidative chemistries that are compatible with oxygen delignification technologies and oxidize the side chain of lignin.

Although the introduction of carboxylic acid groups into residual lignin is undoubtedly a favorable delignification reaction, our results would seem to suggest that this needs to be accomplished with fragmentation of the lignin macrocyclic polymer. This requirement undoubtedly comes about due to the presence of lignin-carbohydrate complexes[44] that in essence tie the lignin polymer to the cellulose polymer.

The improved reactivity of syringyl groups under both pulping and oxygen delignification conditions provides further incentives to genetic research studies targeted at increasing the amounts of syringyl lignin present in hardwood furnishes. In addition, the low reactivity of hexenuronic acids could be mitigated by developing genetically modified hardwoods that have low and/or no 4-O-methylglucuronic acids. In the interim, a mild pretreatment to remove hexenuronic acids without degrading xylans prior to oxidation delignification would be a promising technology to improve O-bleachability of kraft pulps.

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Chapter VIII. Profiling Oxygen Delignification of Conventional SW Kraft Pulp

Although conventional oxygen delignification has been widely used for lignin removal before bleaching and has become one of the dominant post-kraft pulping delignification technologies for both ECF and TCF operations the changes in lignin content and fiber charge during the process are poorly defined.[1] Fiber charge of chemical pulps is an important chemical property that can affect the binding of metal ions to pulps, fiber swelling, water removal during wet pressing, the rate of refining, the adsorption of retention aids, and the strength and optical properties of the resultant papersheets.[2,3] Carboxylic acid groups in cellulosic fibers are the main functional groups responsible for surface and bulk charge of kraft pulps. Therefore, the introduction of carboxylic acid groups into fiber by direct chemical and enzymatic modification of pulp, such as by grafting or the addition of additives has been extensively studied.[4-14] In contrast, the parameters important to maximizing fiber charge in modern pulping and bleaching operations have only recently begun to be examined.[15-17]

As reported recently, oxygen delignification can enhance or slightly diminish fiber acid group content for softwood kraft pulps.[17-19] An increase in the fiber charge after an O-stage can be attributed, in part, to oxidative depolymerization reactions with lignin.[20, 21] Simultaneously, the reactive oxygen species in an O-stage have been shown to yield aldonic acids[22] that can either enhance overall fiber charge or contribute to pulp yield loss and a reduction in fiber charge. Therefore, changes in fiber charge after oxygen delignification are anticipated to depend on process conditions and this has not been fully investigated. Additionally, the kinetic changes in fiber carboxylic acid content and its distribution between residual lignin and the carbohydrate fraction during oxygen delignification remain ill-defined and require further investigation. This study examines the changes in fiber charge during oxygen delignification of a SW kraft brownstock pulp and establishes to what extent this charge is associated with lignin and pulp carbohydrates.

Chapter VIII. Experimental

Materials.   A commercial southern U.S.A pine kraft pulp with a kappa number of 32.5 was used for oxygen delignification studies. All other chemicals and solvents were commercially purchased and used as received with the exception of 1, 4-dioxane which was freshly distilled over $NaBH_4$ prior to use.

Oxygen delignification.   All one stage oxygen delignification experiments were conducted in a 1 liter inclined rotary stirred Parr reactor filled with 30.00 oven dry (O.D.) grams of pulp at 10% consistency. $MgSO_4$ was charged to the reactor so that the molar ratio of Mg/Mn in the pulp was kept at 30-33: 1 mol/mol to offset the detrimental effects of Mn^{2+}.[23]   The varied experimental parameters include: NaOH: 1.5, 2.5, and 3.5%; temperature: 85, 100, and 115˚C; oxygen pressure: 640, 800, and 960 kPa, and reaction time: 10, 20, 30, 45, 60, and 80 minutes. The oxygen delignified pulps were washed and air dried or stored at 2 ˚C prior to analysis.

Holopulping.   The oxygen delignified pulp was holocellulose pulped (holopulp) following the procedure outlined below. In brief, pulp samples (2.00 g) were dispersed into 75.00 ml deionized water, treated with 0.50 ml glacial acetic acid and 0.60 g of $NaClO_2$. The resulting mixture was warmed to 75 $^{\circ}$C. After stirring for 1 hour, additional glacial acetic acid (0.50 ml) and $NaClO_2$ (0.60 g) were added and the reaction was continued for another 1 hour. This process was repeated for a total of 3 hours. The treated pulp was then cooled to 0 $^{\circ}$C, filtered, washed using deionized water and air dried for further determination.

Analytical Methods. Metal ion concentration in pulp samples were analyzed using inductively coupled plasma emission spectroscopy following literature methods.[24,25] The carboxylic acid content in samples was determined using Head Space Gas Chromatography (HSGC) [26] and hexenuronic acid (HexA) in pulps was determined using a spectroscopic method.[27] Residual lignin was isolated from pulp by employing a mild acid hydrolysis procedure that had been described in the literature.[28]

In addition, TAPPI standard methods[29] were used to determine pulp kappa number (T236 cm-85), pulp brightness (T452 om-92), pulp viscosity (T230 om-94), and paper sheet tensile strength (T404 om-87). Fiber length was measured by using Fiber Quality Analyzer.[30]   The standard deviation at 95% confidential level was used for the experimental error evaluation for all of these measurements.

Chapter VIII. Results and Discussion
Profiling carboxylic acid – lignin content in oxygen delignified fiber.   A series of oxygen delignification experiments were conducted at varied reaction times, oxygen pressures, caustic charges, and temperatures. The development of total carboxylic acid content in oxygen delignified pulps is summarized in Figure VIII.1-2.

(a)

(b)
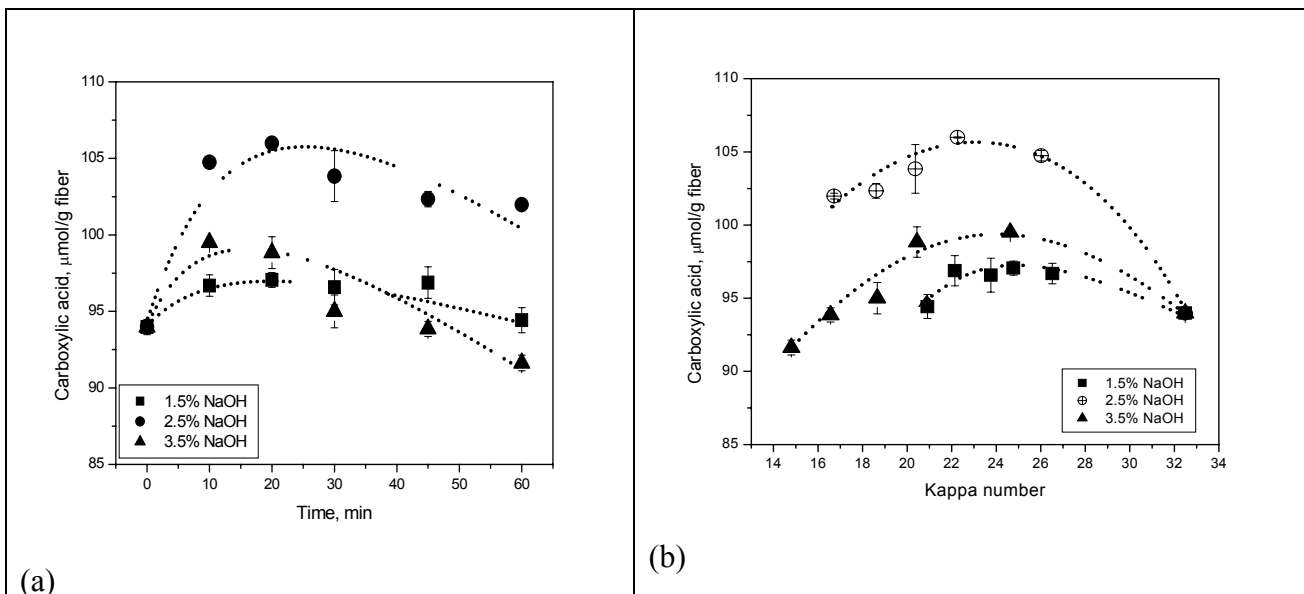
Figure VIII.1.   Total fiber carboxylic acid content development at different initial alkalinity   (NaOH: 1.5, 2.5, 3.5%; temperature: 100 $^{\circ}$C; O_2 pressure: 800 kPa)

From Figure VIII.1a, two distinct phases exist for the total fiber carboxylic acid content profile in oxygen delignified pulps: an initial 4-13% rise in the first 10-30 minutes is followed by a slow decrease phase under different initial alkalinity. Figure VIII.1b showed the maximum total fiber carboxylic acid content occurs at a kappa number of 21-24 and further delignification is obviously not beneficial to total fiber acid increase.
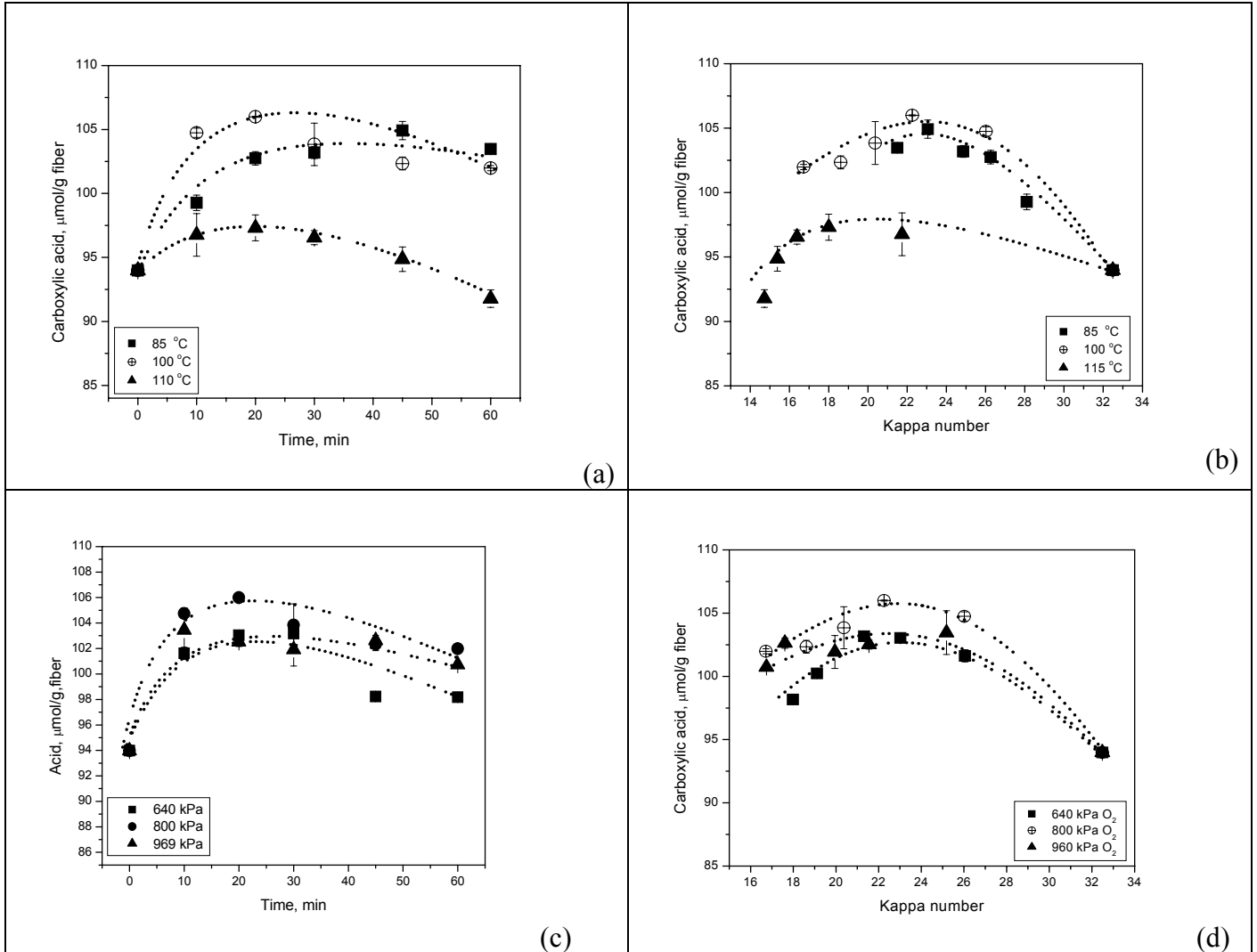
Figure VIII.2. Total carboxylic acid content development in oxygen delignified pulps at different temperatures (a-b) and oxygen pressure (c-d)
a-b: Temperature: 85, 100, 115 ˚C; NaOH: 2.5%; O_2 pressure: 800 kPa
c-d: O_2 pressure: 640, 800, 960 kPa; NaOH: 2.5%; temperature: 100 ˚C

The same profile for total fiber carboxylic acid content was also found in oxygen delignified pulps at different temperatures and oxygen pressure as shown in Figure VIII.2. Similarly, the maximum total fiber carboxylic acid content was found at a kappa

number of 19 - 24 under different reaction temperatures (Figure 2b) and varied oxygen pressure (Figure VIII.2d).

Previous oxygen delignification studies[31] have shown that residual lignin exhibits a rapid initial degradation followed by a slower delignification phase. The oxidized residual lignin in the pulp will contribute to fiber charge of oxygen delignified pulps. Likely, cellulosic and hemicellulose aldolic acids formed during oxygen delignification are also a source of fiber charge for oxygen delignified pulps. Therefore, the total fiber carboxylic acid content in oxygen delignified pulps results from the formation of carboxylic acids in different chemical components of the fiber. The two-phase development for total fiber carboxylic acid of oxygen delignified pulps should be ascribed to different acid groups from these chemical components in each phase.

As shown in the literature,[31] the degree of delignification increases with alkalinity and/or reaction temperature. However, Figures VIII.1-2 show that higher NaOH (3.5%) and higher temperature (115°C) did not result in higher total fiber carboxylic acid content in oxygen delignified pulps. In addition, oxygen charge shows no significant effect on fiber carboxylic acid development under the experimental conditions studied. The optimal fiber carboxylic acid content for the conditions studied was obtained at 100 °C with 2.5% NaOH and 800 kPa oxygen.

Chemical component contributions to total carboxylic acid content of oxygen delignified pulps

In general, the source of total acid groups in bulk pulp consists of three parts: residual lignin (RL), carbohydrate, and extractives. For oxygen delignified pulps, the contribution from extractives can be considered to be negligible. Therefore, the carboxylic acid in residual lignin and carbohydrate are two major contributors to total fiber acid content in oxygen delignified pulps.

In unbleached kraft pulps, hexenuronic acids (HexA) are an important contributor to fiber charge. However, there are few HexA remaining in oxygen delignified pulps after holopulping due to the ClO_2 (see Table VIII.1). The absolute amounts of hexenuronic acids present in SW and HW kraft pulps has been reported to vary substantially depending on several parameters including wood furnish and pulping parameters.[32] For elemental chlorine free bleaching protocols, it is well established chlorine dioxide readily reacts with hexenuronic acids and these pulps typically contain only small amounts of these unsaturated sugars (<10% of brownstock value of HexA).[33] In this study, we separated the carbohydrate carboxylic acid content in oxygen delignified kraft pulp into two parts: HexA and other aldonic acids in holopulp. As the HexA content does not change during oxygen delignification (see Table VIII.1), accordingly, the acid profile of oxygen delignified pulps will be mainly affected by the carboxylic acid in residual lignin and fiber carbohydrates of the oxygen delignified pulps.

Table VIII.1. HexA in oxygen delignified pulp and corresponding holopulps

| Time, min	0	10	20	30	45	60	average
HexA, μmol/g, O-Pulp*	28.7	27.8	-	28.0	-	28.2	28.2
HexA, μmol/g, holopulp**	3.5	2.9	2.8	2.2	2.0	3.5	2.8

Conditions: NaOH: 2.5%; temperature: 100 ˚C; O_2 pressure: 800 kPa
*   Oxygen delignified pulp, 0.38% standard deviation
** Holocellulose made from oxygen delignified pulp, 0.64% standard deviation

Carboxylic acid content in residual lignin isolated from oxygen delignified pulps

Figure VIII.3 summarizes the change in carboxylic acid groups in residual lignin isolated from oxygen delignified pulps treated at 100 ^{o}C with 2.5% NaOH and 800 kPa O_2. A 37% initial rise for acid group content was observed in the first 10 minutes of oxygen delignification followed by a rapid decrease, after which the carboxylic acid profile exhibited a slow increase phase. The maximum acid group content in lignin occurs at a kappa number of 25. The large increase in the carboxylic acid content of residual lignin in the first 10 minutes can probably be attributed to the oxidation of readily oxidizable residual lignin functional groups.
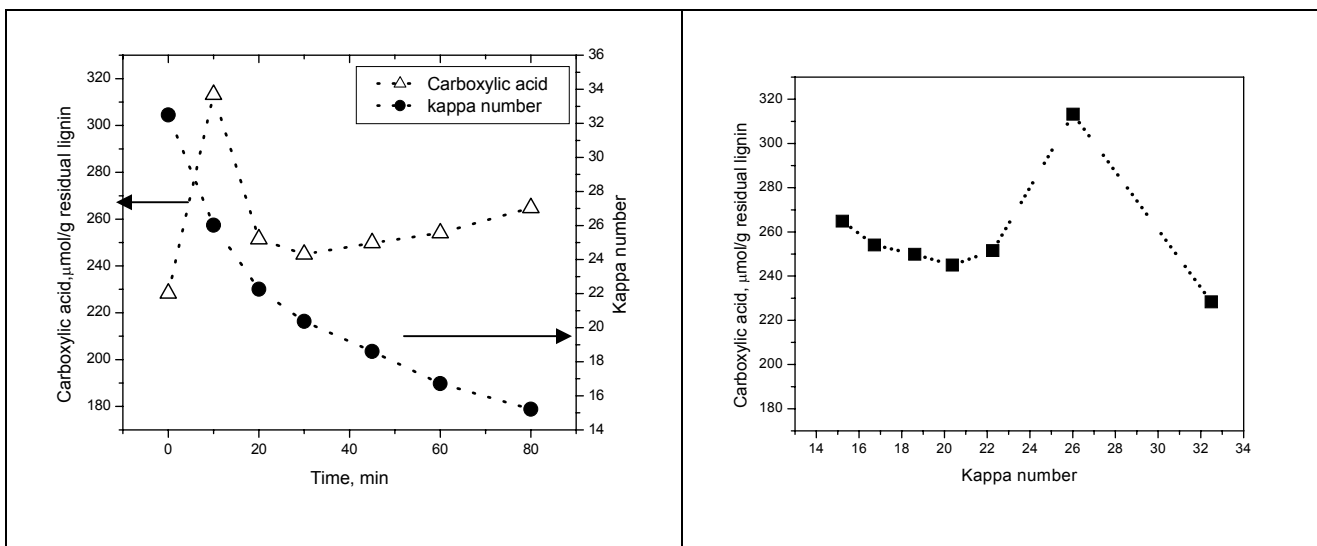
Figure VIII.3. Carboxylic acid content profile in residual lignin during oxygen delignification. Conditions: 2.5% NaOH, 800 kPa O_2,100 ˚C, 0-60 minutes

Time-dependent carboxylic acid profile in holopulps

Despite the changes in carboxylic group content of residual lignin during oxygen delignification, these acids groups do not contribute to the fiber charge of fully bleached pulps since subsequent bleaching stages remove this lignin. Therefore, fiber charge for fully bleached ECF pulp must originate primarily from carboxylic acid groups attached to

polysaccharides. Previous research studie[33] have reported total fiber charges of 56, 51, and 57 µmol/g for softwood kraft pulps bleached via OPZEP, ODEDED and DEDED, respectively. The corresponding kappa numbers/HexA contents for the same fully bleached pulps were 0.8/4.0 µmol/g, 0.4/2.3 µmol/g, and 0.8/3.2 µmol/g respectively. Since the remaining residual lignin and HexA concentrations in these fully bleached pulps are so low, the fiber charge of these pulps must predominantly come from carbohydrates.

In order to investigate the acid group development in carbohydrates during oxygen delignification, instead of fully bleaching the oxygen delignified pulp using ECF or TCF bleaching sequences, the oxygen delignified pulps were holocellulose pulped. These holocellulose pulps were used to evaluate the carboxylic acid charge component of pulps after all lignin is oxidatively removed. Control experiments with a fully bleached pulp indicated that the holocellulose pulping did not result in any additional oxidation to the pulp.

As summarized in Figure VIII.4, three phases of carboxylic acid content appear in oxygen delignified holocellulose pulps. Initially, a 6-8 % of decrease in carbohydrate acid groups is observed during the first 10 minutes of oxygen delignification followed by a small increase and a final leveling off or slight decrease. Profiling the carboxylic acid content in the holocellulose oxygen delignified pulps established that a 6-8% increase in fiber charge occurred after 26-42% oxygen delignification of the pulp. This narrow increase in fiber charge limits the opportunities of engineering dramatic changes in fiber properties via a routine O-stage.

The initial rapid decrease of carboxylic acid occurred most likely because of oxidative degradation of easily accessible hemicellulose and acidic amorphous cellulose. The gradual increase of carboxylic acid content with time should involve direct oxidation of pulp carbohydrates via reactive oxygen species. This reaction is favored in the latter stages of oxygen delignification after the easily oxidizable fragments of lignin are oxidized. The final phase consisting of a flat or slow decrease of acid group formation is thought to be the oxidation and slow elimination of acid groups. These changes are supported by the reported changes of cellulose crystallinity during oxygen delignification.[34]

The results in Figure VIII.4 also indicate that high alkalinity (3.5% NaOH) and high temperature (115 $^\circ$C) do not favor carboxylic acid formation in holocellulose of oxygen delignified pulps. Generally, the appropriate parameters to obtain higher carboxylic acid in holocellulose of oxygen delignified pulps in this study are at 100 $^\circ$C with 1.5% NaOH and 800 kPa oxygen.
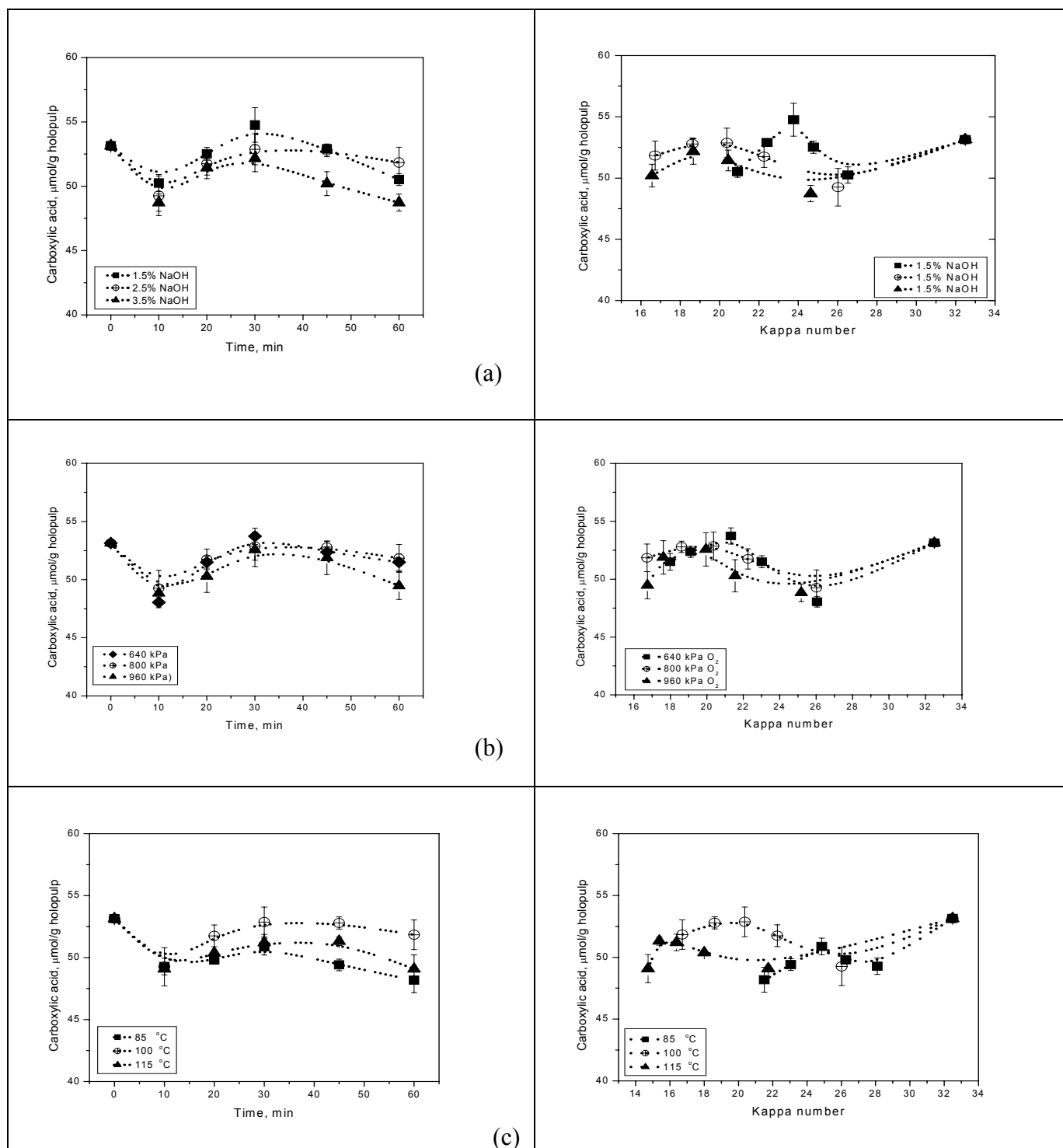
Figure VIII.4. Carboxylic acid in holocellulose of oxygen delignified pulp

a: NaOH: 1.5, 2.5, 3.5%; temperature: 100 ˚C; O_2 pressure: 800 kPa

b: Temperature: 85, 100, 115 ˚C; NaOH: 2.5%; O_2 pressure: 800 kPa

c: O_2 pressure: 640, 800, 960 kPa; NaOH: 2.5%; temperature: 100 ˚C

As already discussed, the total fiber carboxylic acid profile during oxygen delignification

is mainly influenced by the carboxylic acid content of residual lignin and the pulp polysaccharides. Due to the different behavior of residual lignin and pulp polysaccharides in an oxygen delignification stage, the relative contribution of carboxylic acid to total fiber charge from both residual lignin and holocellulose are different.

From Figure VIII.5, it is obvious that the acid groups in residual lignin have a significant effect on total fiber carboxylic acid development in the initial phase and the carboxylic acid profile in carbohydrate fraction of oxygen delignified pulps influences the total fiber charge behavior in the remaining phase.
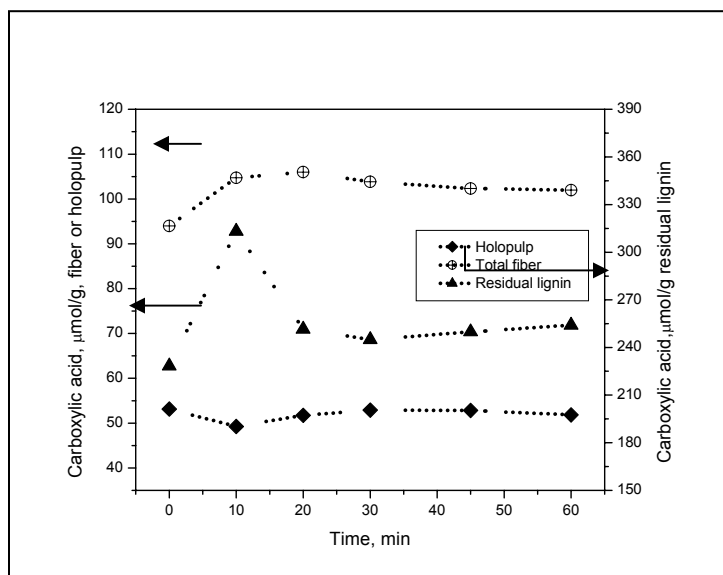
Figure VIII.5. Carboxylic acid content in total pulp fiber, residual lignin and holocellulose of oxygen delignified pulps. Conditions: 2.5% NaOH, 800 kPa O_2,100 ˚C, 0-60 minutes.

Relationship between carboxylic acid content in holocellulose of oxygen delignified pulps and physical sheet strength

As observed in Figure VIII.6 and Table VIII.2, the holocellulose of oxygen delignified pulps with higher carboxylic acid content (55.4 μmol/g holopulp) show higher tensile strength than those with lower carboxylic acid (34.8 and 38.6 μmol/g holocellulose). Since these pulps have comparative viscosity values, the differences in tensile strength were assigned to the difference of carboxylic acid content.
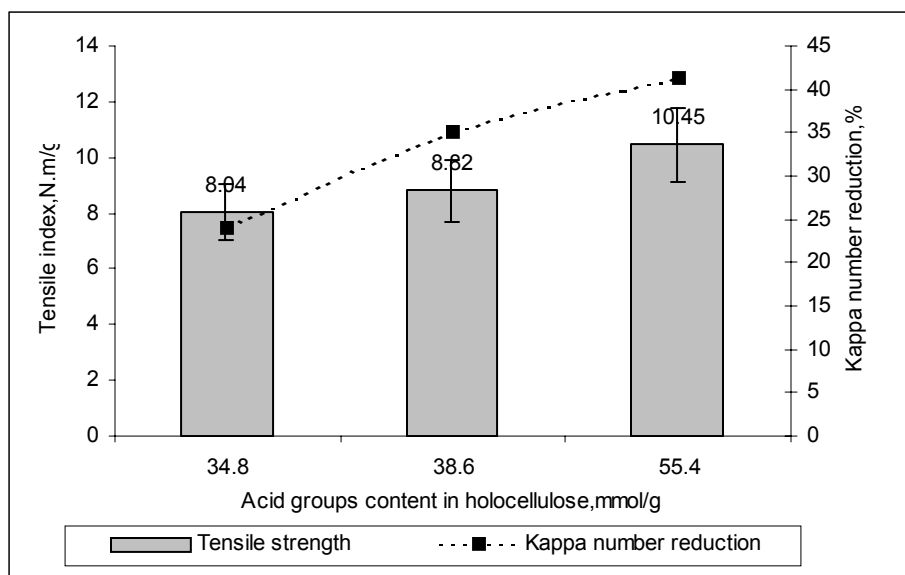
Figure VIII.6. The effect of carboxylic acid in holocellulose of oxygen delignified pulps on sheet strength

Table VIII.2. The holocellulose fiber and paper properties

Carboxylic acid (μmol/g holopulp)	Mean length (Length weighted, mm)	Brightness (%)	Viscosity (mP.s)
34.8	2.39 ±0.03	83.4	11.3
38.6	2.39 ±0.06	83.8	11.1
55.4	2.40 ±0.07	84.0	10.5

Chapter VIII. Conclusions

Based on the experimental results from a series of one stage oxygen delignified pine kraft pulps, the following conclusions on carboxylic acid development in oxygen delignified pulps can be obtained.

- Total fiber carboxylic acid profile exhibited an initial 4-13% increase in the first 10-30 minutes followed by a steady or slight decrease (2-7%).
- Holopulps in oxygen delignified pulps initially exhibited a 6-8% decrease in fiber charge in the first 10 minutes of an O-stage followed by a small increase (3-11%) and finally a slow decline (5-10%).
- The residual lignin exhibited an initial 37% acid group content rise in the first 10 minutes of an O-stage and this was followed by a rapid decrease (16%) and then a slow increase (8%) in the last 50 minutes of oxygen delignification.
- The maximum carboxylic acid content for the pulp and holocellulose from oxygen delignified pulps during oxygen delignification occurred after 26-42% delignification.

- For the oxygen delignification conditions studied, fiber charge was maximized employing a reactor temperature of 100 ^{0}C with 2.5% NaOH and 800 kPa oxygen.

These results suggest that acid groups in the carbohydrate fraction of softwood kraft pulps are formed and removed during an O-stage, concurrently. The dominant effect will determine the final carboxylic acid in the pulp carbohydrate. However, the overall increase of carboxylic acid groups in total pulp fiber and carbohydrate fraction is limited. Therefore, future studies in this program will examine the development of selective catalysts and/or modified process parameters to further increase the acid group content in pulp carbohydrates.

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Chapter IX. Profiling Oxygen Delignification of High-Kappa SW Kraft Pulp

Extended oxygen delignification technology provides a simple and selective approach to produce high brightness bleached kraft pulps from high kappa kraft pulps. This has been recently described by Poukka et al. as the integration of high kappa cooking and extended oxygen delignification into the fiber line.[1] Recently, an issue of increasing practical interest is the changes in fiber charge for oxygen delignified pulps.[2,3] It is known that carboxylic acid groups are the main groups responsible for bulk and surface fiber charge of kraft pulps, which can impact ion-exchange properties and fiber swelling ability. These effects influence fiber flexibility, inter-fiber bonding during pressing and drying operations, as well as paper sheet mechanical properties.[4,5,6] In oxygen delignified kraft pulps, the change in the carboxylic acid content is primarily associated with the oxidation in residual lignin and polysaccharides.[7,8] Varying the cooking conditions not only affects the final pulp kappa number but also results in different structural properties for residual lignin and hemicellulose. Studies described in chapter VIII demonstrated that a conventional pulp with a kappa number of 32.5 will result in 4-13 % increases in total fiber charge and 6-8% increase in the polysaccharide component of kraft pulps after 26-42 % delignification depending on process conditions. This paper elucidates the changes in carboxylic acid content for high kappa SW kraft pulps before and after extended oxygen delignification.

Chapter IX. Experimental

Materials. Air dried screened southern pine wood chips from a commercial U.S. kraft pulp mill were used for the pulping studies. The two SW kraft pulps with a kappa number of 49.5 and 48.0 were prepared by cooking in a M&K digester at a 15% and 19% active alkali charges with 1650 and 1050 H-factors respectively while keeping sulfidity at 25% and cooking temperature at 170° C with a liquid/wood ratio of 4:1. After kraft pulping, the pulps were disintegrated, screened, and washed thoroughly with water and stored at 2 °C.

Oxygen Delignification. One- and two-stage oxygen delignification experiments were conducted using a Parr reactor. In a typical oxygen delignification experiment, the reactor was preheated and charged with kraft pulp (100 g o.d.) and the consistency was adjusted to 10% using deionized water with 0.05% $MgSO_4$ and varying amounts of NaOH as summarized in Table IX.1. After sealing the reactor, the vessel was heated to the desired temperature (70–110°C) and pressurized with O_2 (40 psi). The reaction was terminated after 60 minutes and the O_2 pressure was released. The pulps were then washed, air dried, and analyzed for pulp properties. For the OO- stage experiment, the pulp was washed with deionized water between the first and second stage.

Table IX.1. Oxygen delignified pulp properties

Sample	NaOH (%)	Temperature (^{o}C)	Kappa number	Viscosity (mP.s)
LSW	-	-	49.5	36.8
LO	3.0	90	30.0	27.0
LOO1	3.0	70	25.0	25.2
LOO2	4.4	76	22.0	23.0
LOO3	1.6	105	19.3	20.2
LOO4	3.0	110	14.3	15.7
HSW	-	-	48.0	29.0
HO	3.0	80	31.0	25.0
HOO1	3.0	70	26.0	24.0
HOO2	1.0	90	24.0	23.0
HOO3	5.0	90	20.3	18.2
HOO4	3.0	110	14.8	14.5

LSW and HSW: Unbleached SW kraft pulp cooked at low AA and high AA, respectfully.
LO and HO: 1st stage oxygen delignification for LSW and HSW, respectfully.
LOO1-LOO4 and HOO1-LOO4: a series of 2nd stage oxygen delignification for LO and HO, respectfully.

Holopulping. The oxygen delignified pulps were holocellulose pulped (holopulp) following literature methods (Zhang, et al. 2005). In brief, pulp samples (2.00 g) were dispersed into 75.00 ml deionized water, treated with 0.50 ml glacial acetic acid and 0.60 g of $NaClO_2$. The resulting mixture was heated to 75 ^{o}C. After stirring for 1 hour, additional glacial acetic acid (0.50 ml) and $NaClO_2$ (0.60 g) were added and the reaction was continued for another 1 hour. This process was repeated for a total of 3 hours. The treated pulp was then cooled to 0 ^{o}C, filtered, washed using deionized water and air dried for further determination.

Pulp Sugar Analysis. Pulp samples were grounded to pass through a 40-mesh screen and hydrolyzed with 72% sulfuric acid for 1 hour at 30 °C, then with 3% H_2SO_4 at 120 °C for 1 hour. The filtrate was analyzed for sugars composition with High Performance Anion-exchange Chromatography (HAPEC) equipped with a pulsed amperometric detector (PAD) on an ion-exchange CarboPac PA-10 column using a Dionex DX-500 system. Fucose was used as the internal standard. Prior to injection, samples were filtered through 0.45 um filter. Sample was eluted with 2.00 mM NaOH as effluent at a flow rate of 1 mL/min, with a post-column addition of 500.00 mM NaOH prior to detection.

Lignin Isolation. Isolation of residual lignin from the kraft brownstocks, O-, and OO- delignified pulps was accomplished employing standard literature methods.[9] In brief, air-dried pulp (30 – 50 g oven dry weight) was added to an aqueous 0.10 N HCl p-

dioxane/water (9:1) solution yielding a final consistency of 4%. The pulp slurry was refluxed for 2 hr under an argon atmosphere, then cooled, filtered, and concentrated under reduced pressure. The precipitated lignin was isolated by ultracentrifuge, washed with acidic water (pH 2~3), 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, corrected for hexenuronic acid content.

^{13}C and ^{31}P NMR Analysis. All NMR spectra were recorded on a 400 MHz Bruker Advance/DMX NMR spectrometer. Quantitative ^{13}C NMR spectra were acquired by using DMSO as solvent for lignin with an inverse gated decoupling sequence, 90° pulse angle, 12-s pulse delay, and 10,000 scans.[9] The integration and carbon content calculation of the functional groups in the ^{13}C NMR spectra were performed in accordance with the literature method.[10] The 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.[9]

Cyclohexanol was used as the internal standard. ^{31}P NMR spectra were recorded using an inverse gated decoupling sequence, 90° pulse angle, 25-s pulse delay, and 150 transients, at room temperature. The integration regions for hydroxyl groups were in accordance with the literature methods.[9] All the NMR spectral acquisition and analyses were controlled by Bruker's XWINNMR 2.6 software running on an SGI (Silicon Graphics Indigo) server using the Irix 7.0 operating system.

Carboxylic acid and Hexenuronic Acid determination. The carboxylic acid content in samples was determined using Head Space Gas Chromatography (HSGC)[11] and hexenuronic acid (HexA) in pulps was determined using a spectroscopic method.[12] The deviation of the measurements was determined using 95% confidential level.

Pulp Analysis. Kappa number was measured according to TAPPI Method um-246. Typical experimental standard deviations for this procedure were determined to be ±0.5% for the high kappa pulps. Pulp viscosity were determined in accordance with TAPPI Standard T-230 om-89 and standard deviation for this measurement was ±1.5(T231cm-96 2002).

Chapter IX.   Results and Discussion

Total fiber carboxylic acid

For unbleached kraft pulps and the corresponding oxygen delignified pulps, residual lignin and pulp polysaccharides are the predominant constituents that contribute to fiber charge. The relationship between fiber charge and extended oxygen delignification of high kappa kraft pulps has not been established. To address this issue, two SW kraft pulps with kappa numbers of 49.5 and 48.0 were prepared by conventional batch cooking with low AA and high AA. These pulps were then oxygen delignified to kappa number values of 26.0-14.4. The pulp properties of oxygen delignified pulps are shown in Table IX.1. The carboxylic acid content for the two kraft SW pulps and the oxygen delignified pulps were determined and these results are summarized in Figure IX.1.
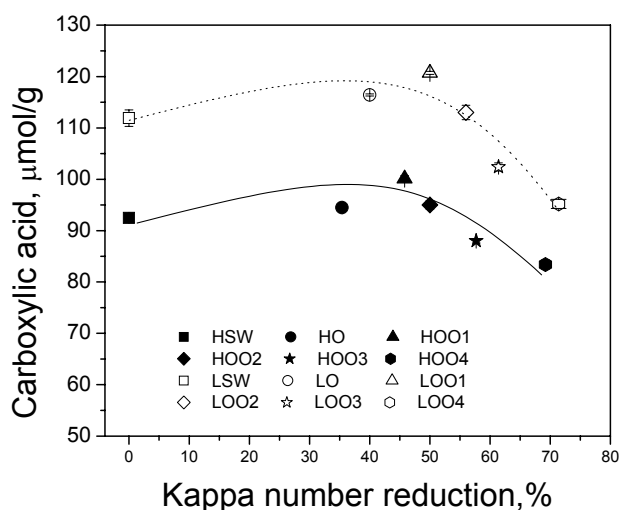
Figure IX. 1. Total carboxylic acid content in oxygen delignified pulps

It is observed that after the first stage of oxygen delignification, total fiber carboxylic acid content for both low AA and high AA cooked SW kraft pulps increased by 2-4%. However, further delignification via a second O-stage either slightly increases or decreases total fiber carboxylic acid content, depending on the degree of lignin removal, which is caused by either high caustic charge or high temperature or the combination of both. Generally, following the first O-stage, an additional 10-35% delignification by a second O- stage leads to 3-18% decrease for total fiber carboxylic acid content. It is also interested to note that the carboxylic acid content in low AA cooked SW kraft pulp and the corresponding O- and OO- delignified pulps was 13-23% higher than that in high AA cooked SW kraft pulp and the corresponding O- and OO- pulps.

Since the polysaccharide and the residual lignin are the main chemical components to contribute carboxylic acid groups to fiber charge of kraft pulps and oxygen delignified pulps, it is interesting to determine how the extend oxygen delignification influences the carboxylic acid group formation in these components.

Carboxylic acid in polysaccharide
Based on oxygen delignification chemistry, pulp carbohydrates are known to experience two main types of reactions. One is degradation, the well known alkaline peeling reaction (see Figure IX.2) due to the oxidative formation of a C-2 carbonyl group on the cellulose chain. The second, is the oxidative stopping reaction as summarized in Figure IX.[7,8]
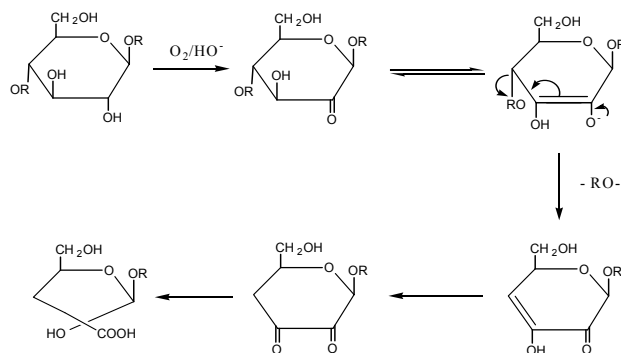
**Figure IX.2**. A mechanism of polysaccharide degradation
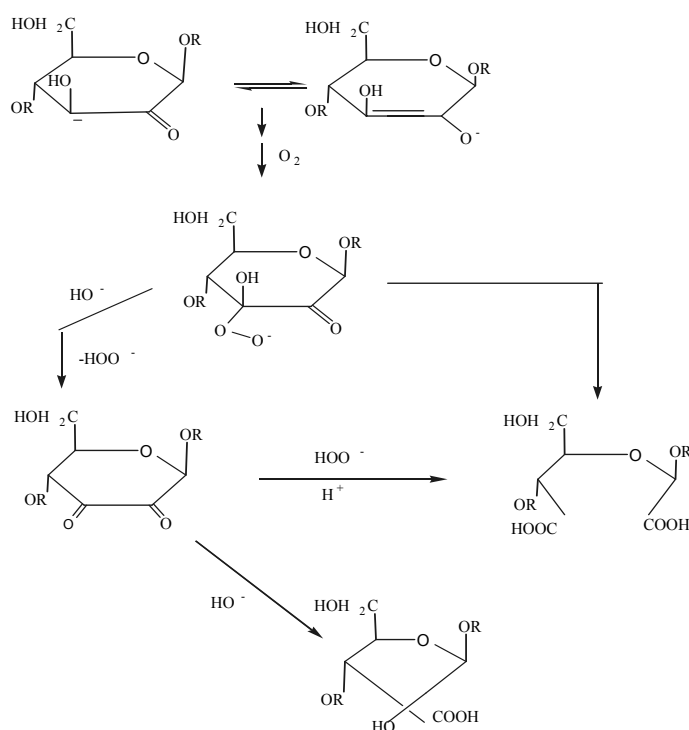
Figure IX.3. A mechanism of polysaccharide oxidative stabilization

Both reactions pathways yield aldonic acids which are a source of new polysaccharide fiber charge for post-delignified pulps. Polysaccharide fiber charge is tremendous practical interest since this represents the primary source of charge for fully bleached pulps. Furthermore, for fully bleached ECF pulps the charge due to hexenuronic acid plays a negligible role. Hence, to evaluate polysaccharide fiber charge before and after an oxygen stage we have utilized holocellulose pulping which oxidatively removes residual

lignin and hexenuronic acid components from the pulp.

Figure IX.4 demonstrates the carboxylic acid content in the holocellulose of one- and two-stage oxygen delignified SW kraft pulps. The data in Figure IX.4 indicates that the carboxylic acid content in the polysaccharide of low AA cooked kraft pulp and corresponding oxygen delignified pulps are 4-9% higher than that of high AA cooked kraft pulp and the corresponding oxygen delignified pulps. Generally, the carboxylic acid content in the holocellulose pulps decreases by 12-26% during oxygen delignification in a near linear relationship with lignin removal for both low AA and high AA cooked pulps.
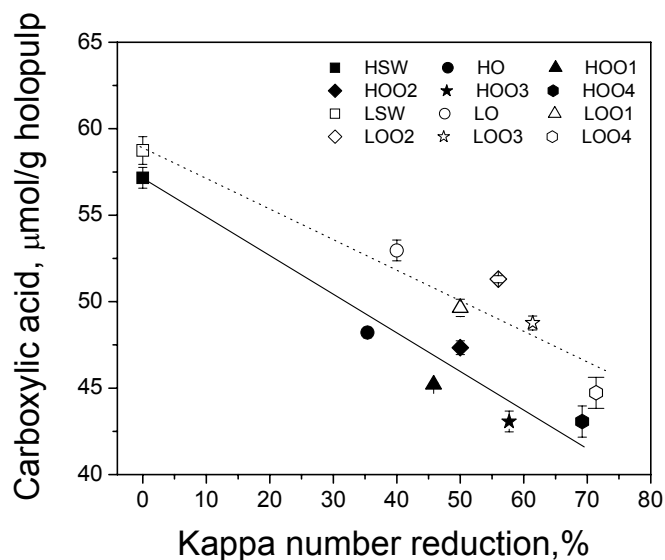
Figure IX.4. Carboxylic acid content in the holocelluloses of one- and two-stage oxygen delignified SW kraft pulps

Carboxylic acid content in residual lignin
The carboxylic acid content in the residual lignin isolated from an O- and OO- stage delignified pulps was determined by quantitative lignin ^{31}P NMR analysis and these results are presented in Figure IX.5. A 50-100% increase in the acid level of the oxidized residual lignin was found after two-stage oxygen delignification for both high AA and low AA cooked SW kraft pulps under the experimental conditions studied.
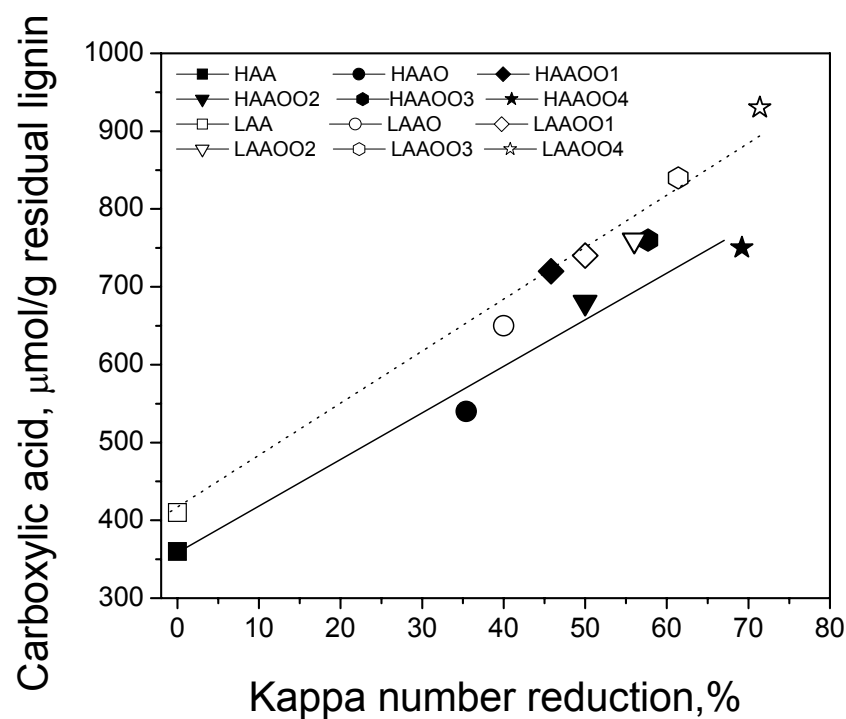
Figure IX.5. Carboxylic acid in the residual lignin of oxygen delignified SW kraft pulps as determined by ^{31}P NMR analysis of residual lignin.

^{13}C NMR analysis of residual lignin isolated from the kraft brownstocks and post-oxygen delignified pulps provided a facile means of measuring the ratio of conjugated: unconjugated carboxylic acids as shown in Figure IX.6.
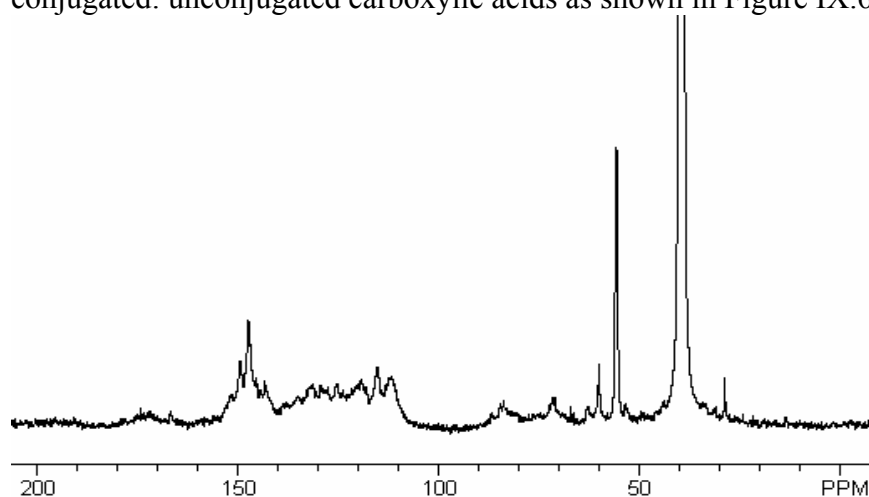
Figure IX.6. Typical ^{13}C NMR spectra of isolated residual lignin in oxygen delignified kraft SW pulps.

It is known that conjugated carboxylic acids can be formed by the oxidative attack of oxygen species toward phenolic moieties in residual lignin to cause aromatic ring opening and generate muconic acids under alkaline conditions (Figure IX.7) and the cleavage of the C_α-C_β linkage of etherified structures containing μ-carbonyl group to form benzylic-type carboxylic acids (see Figure IX.8).[13]
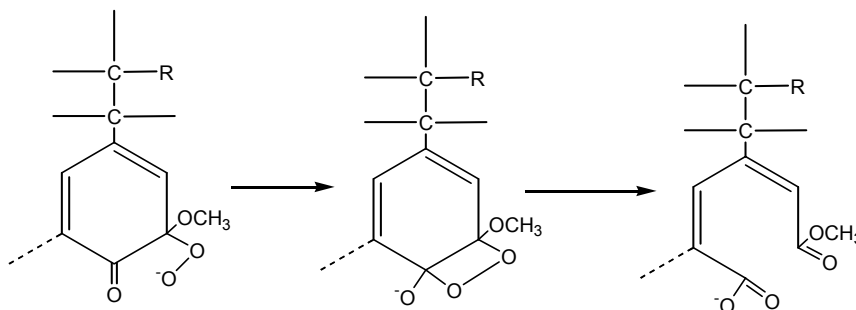
Figure IX.7. Muconic acid formation from ring opening
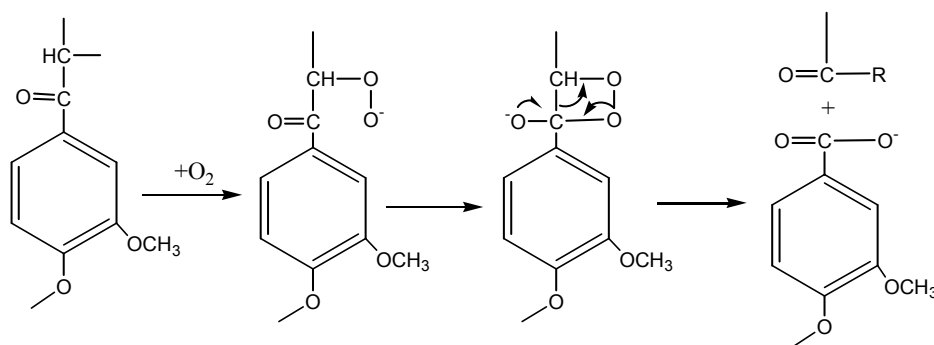
Figure IX.8. Formation of a conjugated carboxylic acid via a side chain cleavage

The ^{13}C NMR spectra data for conjugated and unconjugated carboxylic acids for the residual lignin from post-oxygen delignified pulps are summarized in Figure IX.9.

Figure IX.9. Conjugated and unconjugated carboxylic acids in residual lignin of an O- and OO- stage delignified kraft SW pulps
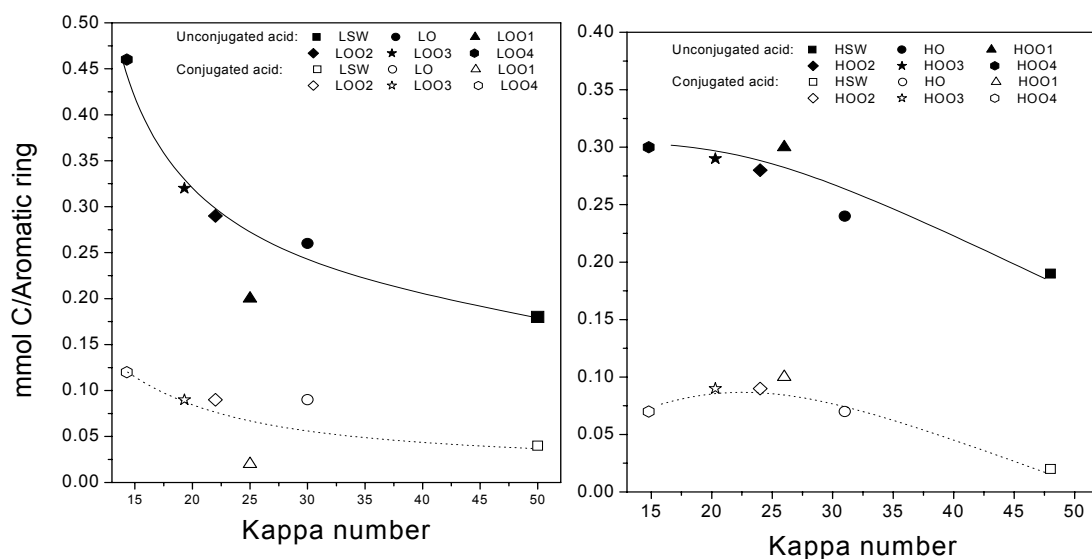
The ^{13}C NMR spectra data (Figure 9) demonstrated that the residual lignin from an O- and OO- stage kraft SW pulps had an increase in carboxylic acids paralleling the results observed with ^{31}P NMR analysis. The residual lignin from the oxygen delignified pulps had a ratio of approximately 3-4:1 for unconjugated to conjugated acid groups. Clearly, the unconjugated carboxylic acid dominates acid functional group in residual lignin of post-oxygen delignified residual lignin, which suggested that most of the muconic acids formed in the residual lignin during an O-stage were further oxidatively fragmented.

Characteristic kappa number for maximum carboxylic acid formation.

As oxygen delignification proceeds, carboxylic acid groups in both the carbohydrate and residual lignin of the pulp will be formed and removed simultaneously under alkaline conditions. As a result, a maximum in pulp carboxylic acid content occurs. Our previous study on an one-stage oxygen delignification of a 32.5 kappa SW kraft pulp indicates that a maximum total fiber carboxylic acid occurs after 24-42% delignification, corresponding to a kappa number of 20-24 (Figure IX.11 b). From Figure IX.11a, under the experimental conditions studied, a maximum for total fiber was observed after 45-50% delignification, which also corresponds to a kappa number of 24-25. These results suggest that a kappa number 20-25 for oxygen delignification of SW kraft pulps can be considered as a characteristic value to obtain a maximum total fiber charge.

(a)   **(b)**
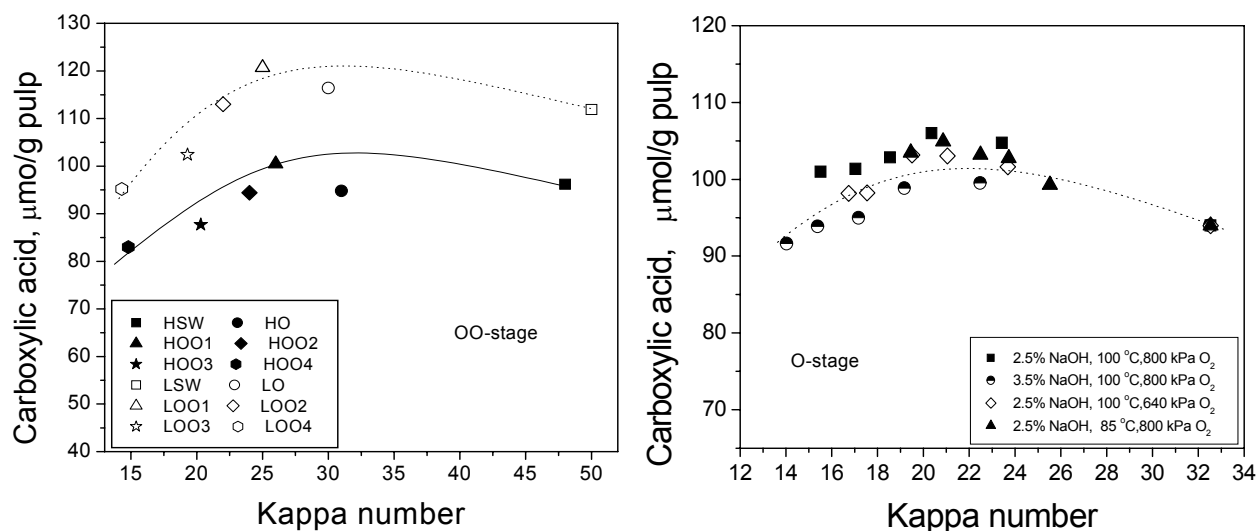
Figure IX.10.   Relationship between carboxylic acid content and kappa number of oxygen delignified pulps for high and conventional kraft pulps

The effect of cooking active alkali on carboxylic acid formation

As expected, hexenuronic acid (HexA) content did not change prior to and after oxygen delignification. However, HexA analysis indicated that low active alkali cooked kraft pulp had higher HexA content (~39.5 μmol/g pulp) than that in high active alkali cooked kraft SW pulp (~28.0 μmol/g pulp). After subtracting HexA from total fiber charge, the remaining carboxylic acid content in low AA cooked kraft SW pulp and corresponding oxygen delignified pulps are still higher (3-10%) than that in high AA cooked kraft SW pulp and the corresponding oxygen delignified pulps (Figure IX.11). The same trend was also observed for acid group content in both holocelluloses. This difference could be contributed to the difference of oxidized hemicellulose retained in both pulps, mainly xylan as illustrated from the sugar analysis shown in Figure IX.12.
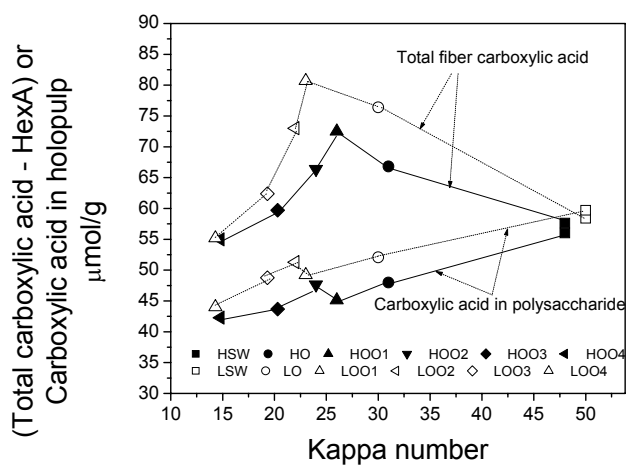
Figure IX.11. The effect of cooking active alkali on carboxylic acid formation in an O- and OO- delignified pulps
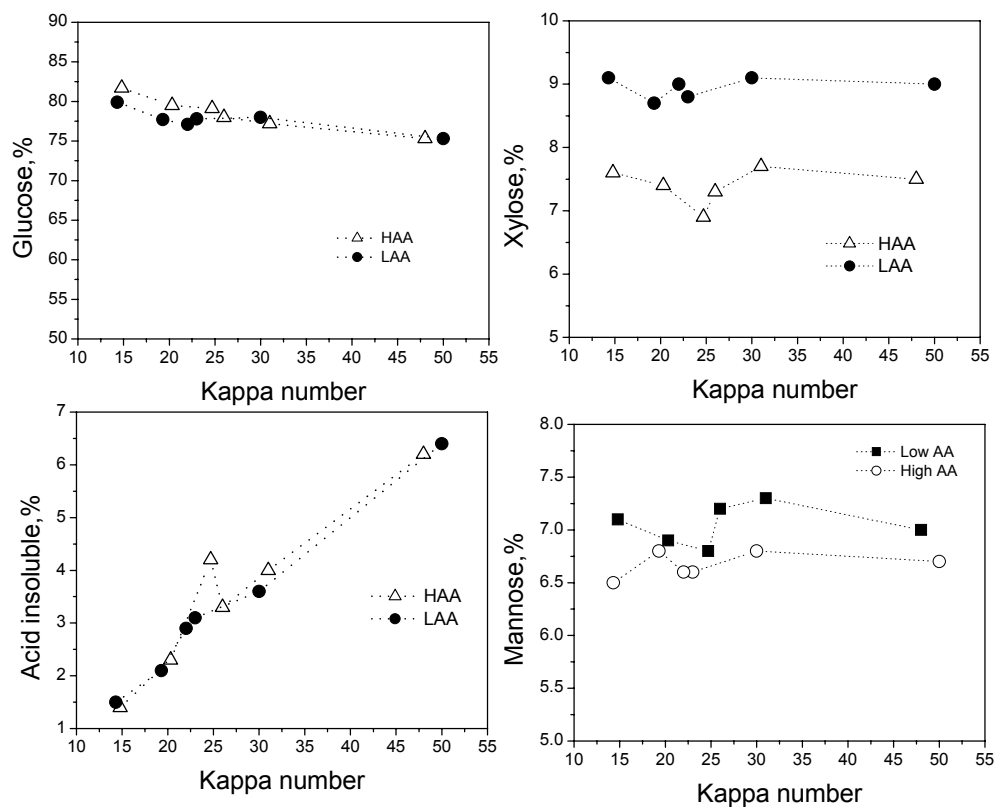
Figure IX.12. The sugar composition in low AA and high AA cooked SW kraft pulps and the corresponding oxygen delignified pulps

Chapter IX. Conclusions

This study examines the carboxylic acid formation during an O- and OO- stage delignification for both high AA and low AA cooked SW kraft pulps. The results demonstrated that the first stage oxygen delignification increased total fiber carboxylic acid content by 2-4% and further delignification via a second O-stage either slightly increased or decreased the fiber carboxylic acid content depending on the degree of lignin removal. Following first O-stage, additional 10-35% delignification from a second O-stage decreased fiber carboxylic acid content by 3-18%. The carboxylic acid group content in corresponding polysaccharides decreases by 12-26% with the extent of O- and OO- stage delignification for both high AA and low AA cooked SW kraft pulps. However, a 50-100% increase of carboxylic acid content in residual lignin of oxygen delignified pulps was obtained after two stage oxygen delignification. The residual lignin from the oxygen delignified pulps had an approximately 3-4:1 of unconjugated to conjugated acid groups. Generally, the carboxylic acid content in low AA cooked SW kraft pulp and corresponding oxygen delignified pulps are systematically higher (3-10%) than that in high AA cooked SW kraft pulp and the corresponding oxygen delignified pulps, which is mainly caused by the difference of hemicellulose (mainly xylan) retained in these pulps. The experimental results also demonstrate that maximum acid content in total fiber occurs at a kappa number of 24-25, which can be considered as a characteristic value for the oxygen delignification to obtain a maximum carboxylic acid groups in total fiber.

Chapter IX. References

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Chapter X.   Predicting Pulp Yields from Oxygen Delignification by Near-Infrared Spectroscopy and Chemometrics

The advances in near-infrared (NIR) spectroscopy and chemometrics analysis have combined to provide a powerful practical technology for a host of process chemistry applications. An examination of the literature demonstrates the application NIR spectrometry for several industries including chemical,[1] food,[2,3] pharmaceutical,[4] and polymer[5,6] applications. These applications are being pursued in-light of several practical advantages for NIR on-line/at-line process analysis. For example, NIR spectroscopy readily facilitates nondestructive in-situ testing with a non-contact probe and optical fiber. The ability to characterize liquid and solid samples with little or no pretreatment, provide quick spectral data and predict physical and chemical parameters from a single spectrum ensure its continuing application as a powerful process analytical tool.

The burgeoning field of biomass processing either for conventional pulp and paper and biofuels-biochemicals processes can clearly benefit from NIR spectroscopy and analysis. The chemical characterization of fibrous biomass with its multi-component chemical constituents provides a challenge few other analytical methods can characterize on an on-line manner. Sanderson et al.[7] demonstrated that NIR could be employed for analysis of lignocellulosics from a broad range of biomass feedstocks. This data was employed to yield a technique that could be useful for rapid chemical analysis of biomass feedstocks for research and industry. Subsequent studies by Kelly et al.[8] showed that both this technique coupled with multivariate analysis techniques could be used to predict the chemical composition of disparate agricultural biomass samples.

The benefits of characterizing biomass have drawn the attention of several researchers in the forest products sector. The application of NIR has been developed into a unique methodology to characterize the chemical,[9,10] physical[11,12] and mechanical[13] properties of wood, pulp and paper. Fardim et al. and others have employed near-IR spectroscopy and multivariate data analysis to develop predictive models for the chemical composition and physicochemical characteristics of unbleached and bleached kraft pulps.[14-17] This analytical procedure has facilitated rapid spectroscopic determination of pulp viscosity, kappa number, pulp brightness values, and pulp content of glucan, xylan, uronic acids, and lignin. Although most of these studies have been directed at laboratory studies, recent research activities at characterizing mill-cooking liquors have demonstrated the application of these technologies for novel mill process sensors.[18]

A key parameter in the delignification and bleaching of pulp is yield. Indeed, over the past decade research has been increasingly directed at improving the selectivity oxygen delignification of kraft pulps. Oxygen delignification employs sodium hydroxide, oxygen and elevated temperatures to remove 30-50% of the residual lignin in kraft pulps. Oxidative degradation of lignin is initiated by single electron reactions between oxygen and the phenolate radical of lignin. Although additional lignin can be removed, the chemical selectivity between lignin and pulp polysaccharides begins to decrease with extended oxygen delignification protocols resulting in decreased pulp yield and lower physical strength properties.   The challenge of monitoring pulp yields for a ~1000

tons/day oxygen delignification reactor have hindered a variety of proposed yield determination protocols.[19,20] This paper summarizes our efforts at developing a novel application of NIR spectroscopy coupled with multivariant analysis to provide a rapid, facile methodology to predict pulp yields for oxygen delignification.

Chapter X. Experimental

Materials. All chemicals were commercially purchased and used as received. A softwood kraft pulp with kappa number 29.4 was acquired from a southern US kraft pulp mill. The pulp was extensively washed until the effluents were colorless and pH neutral.

Oxygen Delignification. Laboratory oxygen delignification studies were conducted in a Parr reactor. In a typical experiment, the reactor was initially warmed up to 70°C. The softwood kraft pulp (80-g od) was then mixed with the desired amount of chemicals and adjusted to 10% consistency with deionized water. After the stock was charged, the reactor was sealed and heated up to a desired temperature under mixing. Oxygen was introduced into the reactor and the pressure was adjusted to 90 psi. After one hour, the reaction was terminated by releasing the O_2 pressure. Pulp was discharged and washed until the effluents were pH neutral and colorless. The oxygen delignification conditions employed are summarized in Table X.1. TAPPI handsheets were then made from the oxygen delignified pulps for NIR measurements. The starting and delignified pulps were analyzed for kappa number following TAPPI Method T 236 cm-85. Typical experimental standard deviations for the preoxygen pulps were determined to be 0.09 and 0.08 for the post oxygen pulps.

Table X.1. Oxygen Delignification Conditions Employed

Temperature, °C	80 – 140
NaOH charge, %	1.00 – 12.00
$MgSO_4$, %	0.05
O_2 pressure, psi	90.0
Consistency, %	10.0
Time, min	60.0

NIR Measurements. Handsheets NIR spectra were measured in the diffuse reflectance mode using Lambda 900 UV/VIS/NIR Spectrometer. Spectra absorbance data are collected at 1.0 nm wavelength internals over the range of 1100 - 2500 nm. The instrument reference was a ceramic standard. Eight scans were taken for each handsheet and thirty two scans were accumulated for each sample and the results were averaged.

Yield Prediction Model Building. Multivariate analysis was carried out by using Unscrambler software developed by CAMO ASA company. Partial Least-Squares (PLS) regression was used to develop the model for oxygen-delignified pulp samples.

Chapter X. Results and Discussion

A series of oxygen delignification experiments were carried out with a softwood kraft brownstock having an initial kappa 29.4. The results of these studies are summarized in Table X.2. As expected, high temperature and alkaline charge generally increased lignin removal. The most drastic conditions examined in this study employed a reaction temperature of 140 ºC and an alkaline charge of 12%. Although these conditions removed 82% of the residual lignin in the pulp it was accompanied with a 13% loss in pulp yield.

Table X.2. Oxygen Delignification of Softwood Kraft Pulp With an
Initial Kappa # of 29

Sample ID	Temperature/ Cº	Alkaline Charge %	Yield %	Kappa #
80-1	80	1.0	99.3	22.0
80-3	80	3.0	97.9	17.9
80-6	80	6.0	97.0	16.4
80-9	80	9.0	98.0	17.8
80-12	80	12.0	97.0	17.9
100-1	100	1.0	97.8	16.7
100-6	100	6.0	95.8	11.7
100-12	100	12.0	95.3	11.6
110-1	110	1.0	98.5	19.1
110-3	110	3.0	96.1	12.0
110-6	110	6.0	92.8	11.4
110-9	110	9.0	92.0	9.1
110-12	110	12.0	91.6	10.8
140-1	140	1.0	94.6	12.3
140-3	140	3.0	91.1	7.6
140-6	140	6.0	90.0	8.1
140-9	140	9.0	88.5	6.3
140-12	140	12.0	86.7	5.4

The brownstock and post-oxygen delignified pulps were analyzed via NIR spectroscopy and representative spectra are presented in Figure X.1. The NIR peaks are broad and the background signal slopes up towards at longer wavelengths due to a dependence of background scattering on wavelength. In general, the absorption bands have been assigned to regions summarized in Table X.3. Bassett and co-workers assigned two of the strongest bands of cellulose, namely those near 1477 nm and 1927 nm to vibrations involving absorbed water.
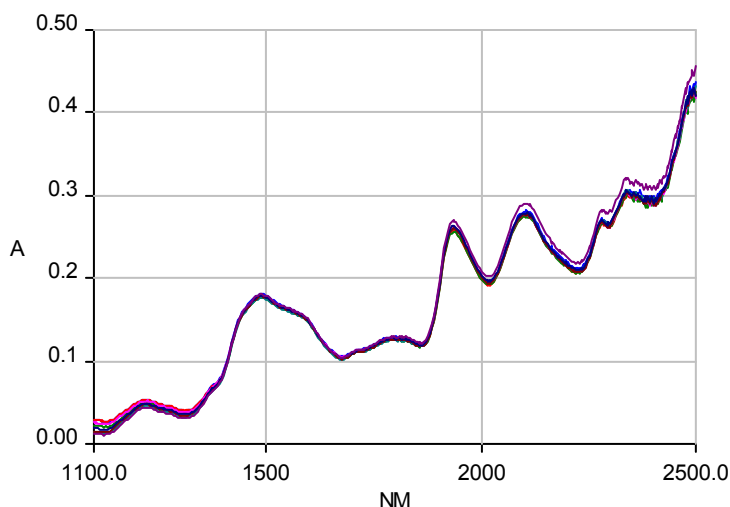
Figure X.1. Representative NIR spectra of oxygen delignified pulp.

Table X.3. Assignments of bands in the region of 2500-1100 nm of the NIR spectrum.

Region/nm	Assignments
2500-1900	Combinations of C-C, C-H, N-H and O-H stretch
1975-1875	2nd Overtone of C=O stretch
1770-1375	1st overtone of C-H, N-H, and O-H stretch and of C-H combinations
1230-1100	2nd overtone of C-H stretch

Statistical Methods

Principle Component Analysis (PCA) is a projection method that helps visualize all the information contained in a data matrix. The principle of PCA is to find the linear combinations of the initial variables that contribute most to make the samples different from each other and to get an approximation of the main systematic variance from a data matrix X. These combinations are called principle components (PCs). The first PC is the one that carries most information and the second PC will then carry the maximum share of the residual information, and so on. PCA decomposes the data matrix X into two small matrices, scores matrix T and loadings matrix P, and an error matrix E. this can be expressed mathematically as:

$$X = T \cdot P^T + E$$

T matrix contains score vectors which describes the sample patterns and generally show sample difference or similarities. P matrix contains loading vectors which describes the variable relationships.

Partial Least-Squares (PLS) regression is also a projection method which models both X and Y matrices simultaneously to find latent variables in X that will predict the latent variables in Y the best. The objective is to maximize the correlation between X and Y, while still maintaining acceptable modeling of the two data sets. The systematic variance

within each block is extracted simultaneously in a way which is similar to PCA. The general form of PLS model can be expressed mathematically as:

$$X = T \cdot P^T + E$$
$$Y = f(X) = T \cdot B + f$$

Where B is regression coefficients, f is Y matrix residuals. In PLS model, the residual is the difference between observed Y value and predicted Y value. Residual Y variance is the variance of the Y residual and expresses how much variation remains in the observed response after taking out the modeled part. Explained Y variance is the complement to residual Y variance, and expressed as a percentage of the total Y variance. Explained variance tells how much of the information in the data matrix is being described by the model. The root mean square error of prediction (RMSEP) measures the prediction error in the same units as the original response variable and tells how large deviations one can expect in the future prediction. PLS1 deals with only one response variable at a time and PLS2 handles several responses simultaneously.

The sample's NIR spectra data were considered as a data matrix X and the PCA procedure was undertaken on the NIR spectra in the range of 1100-2266 nm. As a result, almost 100% of the total variance of the original data can be expressed by 3 principle components (PCs). Figure X.2 shows a plot of variance against PCs. PC1, PC2, and PC3 take into account of 95.8%, 98.4% and 99.2% of total variance, respectively. This analysis indicated that these three principle components fully describe the variance of the X matrix data.
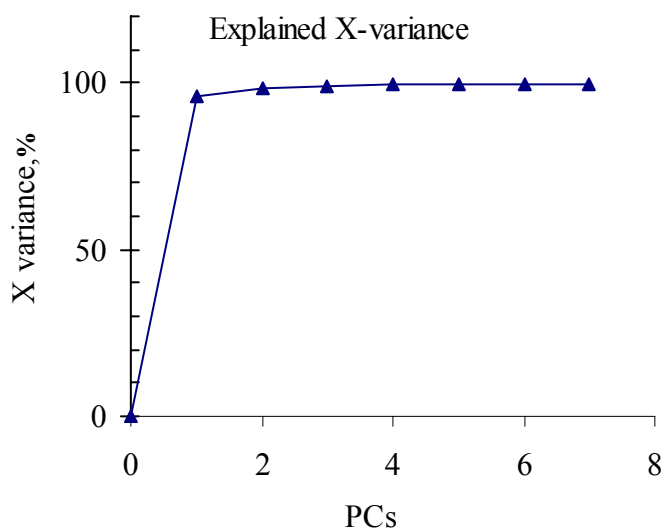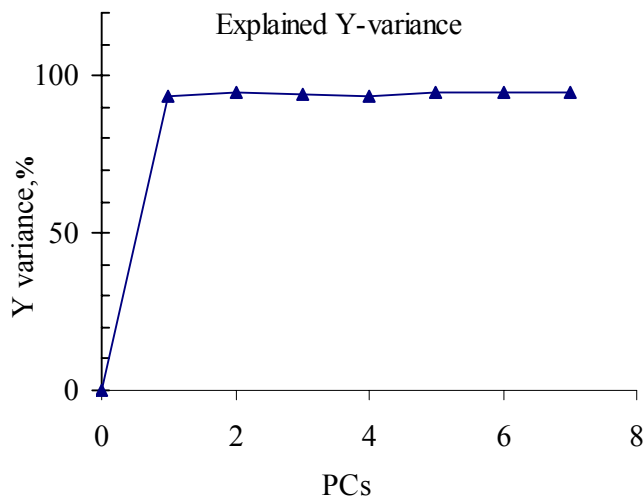

**Figure X.2.** A plot of explained variance versus PCs in the NIR data matrix decomposed by PCA.

PLS regression model of pulp yield

PLS1 modeling was performed by using the NIR data in the range of 1100-2266 nm as a variable X of spectroscopic descriptors and oxygen delignification pulp yield the Y. Twelve post-oxygen delignification pulp samples were used as calibration samples for

building the model and six post oxygen delignification samples were employed as prediction data points. Figure X.3 shows the explained variance of Y variable pulp yield. The first PC explained 93% of the variance. The model describes 95% of the variance for pulp yield at the PC2. The variation cannot be described significantly better with any new PC after the two first PC. This indicates that the model has identified most of the systemic variation when choosing two PCs. The prediction quality of this model is indicated in Figure X.4 and this model has a 0.97 correlation constant. The root mean square error of prediction (RMSEP) has an acceptable low value of 0.56. This indicates that predictions done with this model at two PCs will have an average prediction error of 0.56. The standard error of prediction (SEP) is 0.58.


Figure X.3. Explained variance versus PCs Plot of the PLS1 model for pulp yield prediction based on the NIR data
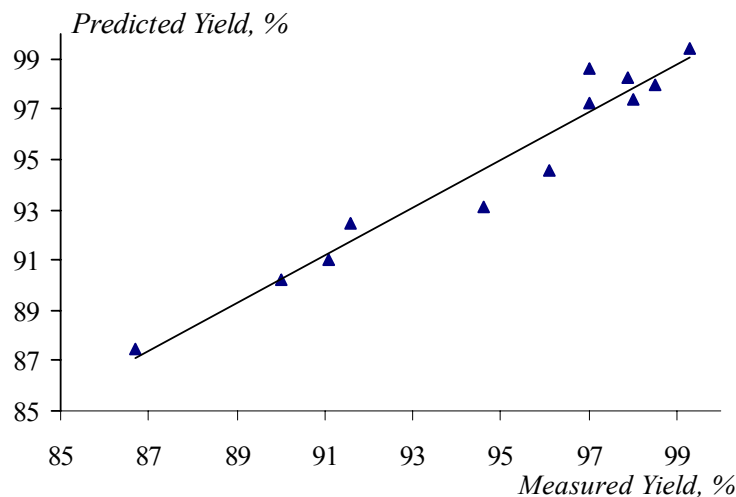
Figure X.4. The predicted vs. measured plot of PLS1 model for pulp yield based on the NIR data with a root mean square error of prediction of 0.56 and standard error of prediction of 0.58.

The NIR spectral data was used to predict pulp yields using the PLS1 model and these results are shown in Figure X.5. This data provided a linear relationship between predicted and actual yield with a 0.92 coefficient. This confirms that this model derived from PLS1 based on the NIR data can be used for the pulp yield prediction in the oxygen delignification.
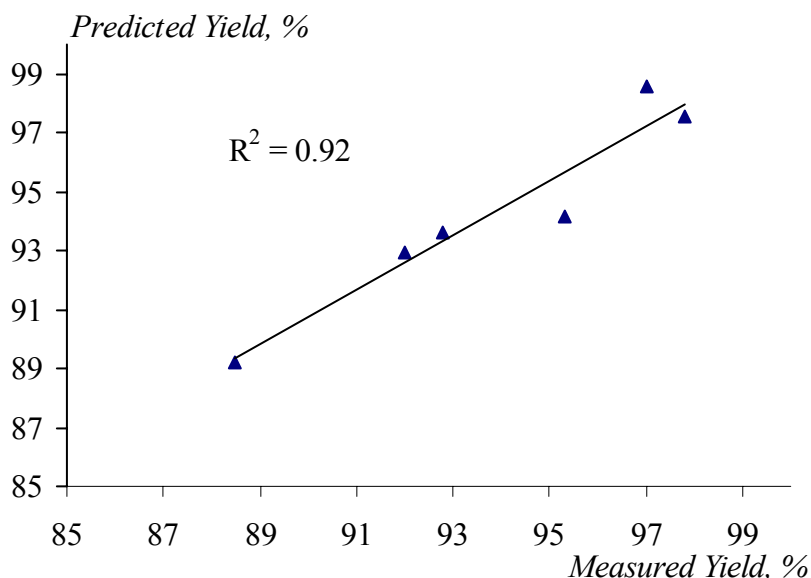
Figure X.5. A correlation between measured and predicted pulp yield with PLS1 model after the oxygen delignification.

Chapter X. Conclusions

The application of NIR and multi-variant analysis provides a rapid and simple method of determining the yield of pulp from an oxygen delignification stage. The analytical methods are relatively straight forward and can be applied employing a low-cost spectrometer. The only necessary requirement for this procedure is the development of sufficient experimental data needed to develop the initial predictive model.

Chapter X. References

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Chapter XI. Oxygen Delignification of Kraft Pulps with Tailored Bleachability Properties

As our prior sections have demonstrated, oxygen delignification is more selective than kraft cooking at kappa numbers corresponding to the final phase of a low kappa kraft cook. However, the drawbacks associated with this process are the capital costs and lower selectivity than chlorine dioxide. Extended oxygen delignification studies indicate that distinct yield benefits can be accomplished by halting the cook at a high kappa number (i.e., 40-50 for SW kraft) before the selectively of the kraft cook decreases in the terminal phase. These observed yield benefits are then further amplified by reducing the organic load on the recovery furnace, resulting in potential productivity benefits for recovery boiler-limited mills.[1] As the incorporation of an-O stage into pulp bleaching operations becomes common practice, an increase in O-selectivity is a very attractive research goal that could improve the overall performance of an O or OO-stage. Hence, kraft pulping, oxygen delignification, and subsequent bleaching processes are all inter-dependent and should be considered on a system approach. This chapter examines the relationship between kraft pulping and extended oxygen delignification and how pulping protocols can influence oxygen delignification pulp bleachability.

Chapter XI. Experimental

Materials. Kraft Pulping Softwood

Screened softwood chips were obtained from a commercial U.S. kraft pulp mill. All kraft cooks were performed in an M&K digester at several alkali charges and H-factors, keeping sulfidity constant at 25% and cooking temperature at 170° C as described in Table XI.1. After kraft pulping, the pulps were disintegrated, screened, and washed thoroughly with water. Kappa number, yield, viscosity, and rejects were measured in each case.

Table XI.1. Softwood pulping to conventional kappa number and high kappa number*.

	Conventional kappa pulping			High kappa pulping		
	Active Alkali (AA)	H- Factor	Kappa	Active Alkali (AA)	H- Factor	Kappa
Low AA	17%	2200	30.0	15%	1650	49.6
Medium AA	19%	1800	30.2	17%	1400	49.5
High AA	21%	1250	30.1	19%	1060	48.0

* temp. 170 °C, sulfidity 25%, liquor/wood 4:1.

Kraft Pulping Hardwood. Screened hardwood chips were obtained from a commercial

U.S. kraft pulp mill. All kraft cooks were performed in an M&K digester at several alkali charges and H-factors keeping sulfidity constant at 25%, as described in Table XI.2. Three hardwood pulps were prepared with a conventional kappa number of 20 and three high lignin content pulps were prepared with a pulp kappa number of 26.

Table XI. 2. Hardwood pulping to conventional kappa number and high kappa number*.

	Conventional kappa pulping			High kappa pulping		
	Active Alkali (AA)	H- Factor	Kappa	Active Alkali (AA)	H- Factor	Kappa
Low AA	14%	1000	19.6	12%	3600	26.8
Medium AA	16%	650	19.3	14%	900	24.2
High AA	18%	500	19.9	16%	550	26.5

*: temp. 170 °C, sulfidity 25%, liquor/wood 4:1.

Oxygen Delignification. One- and two-stage oxygen delignification experiments were conducted using a rotating bomb reactor. In a typical oxygen delignification experiment, the reactor was charged with 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 (1.0 – 5.0%). After sealing the reactor, the vessel was pressurized with O_2 and heated to the desired temperature (70°–110^oC). The reaction was terminated after 1 h, and the reactor was cooled, and the O_2 pressure was released. The pulps were then washed, dried, and analyzed for pulp properties. For the OO stage experiment, the pulp was washed with deionized water between the first and second stage.

Pulp Analyses. Kappa number was measured according to TAPPI Method um-246. Typical experimental standard deviations for this procedure were determined to be ±0.5% for the high kappa pulps. Pulp viscosity values were determined in accordance with TAPPI Standard T-230 om-89 and standard deviation for this measurement was ±1.5.

Chapter XI. Results and Discussion

Influence of Pulping Conditions on Pulp Properties

Softwood kraft pulps with a conventional kappa number of 30 and a high kappa number of 50 were prepared employing different H-factors and active alkali charges (see Table 1). Figures 1 and 2 summarize the pulp yields and viscosity results for these different cooks. The results show that the use of a higher alkali charge in pulping resulted in lower yield and lower viscosity when cooking to the same kappa number for both conventional kappa and high kappa pulps. For example, the kappa 30 pulp cooked with a 15% alkali charge had a yield of 46%, whereas the pulp prepared with 19% alkali charge resulted in

a 43% yield. Low AA pulping provided a 3% improvements in yield in comparison to high AA pulping for kappa 30 pulp, and ~ 4% yield improvement for the kappa 50 pulp. These results suggest that softwood kraft cooking at a lower alkali charge has a better pulping selectivity than at a higher alkali charge.
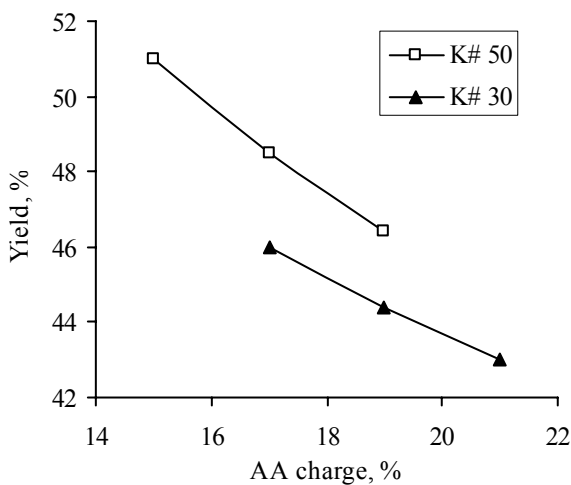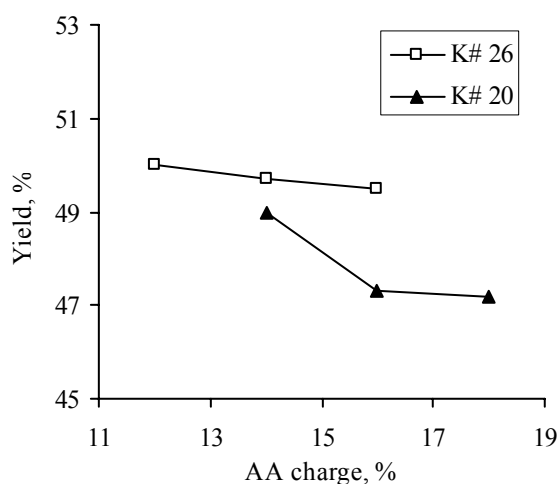

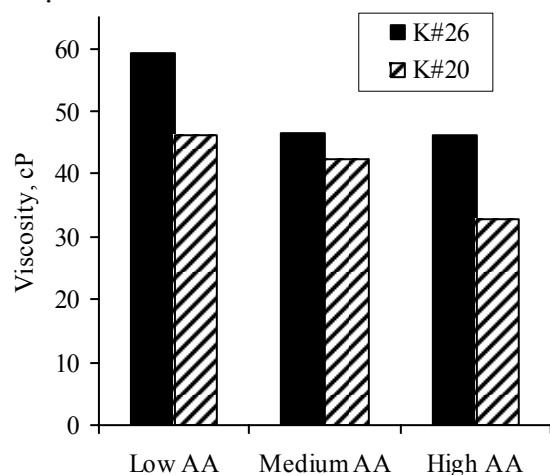**Figure XI.1.** Pulping yield for low, medium and high AA softwood kraft cooking.
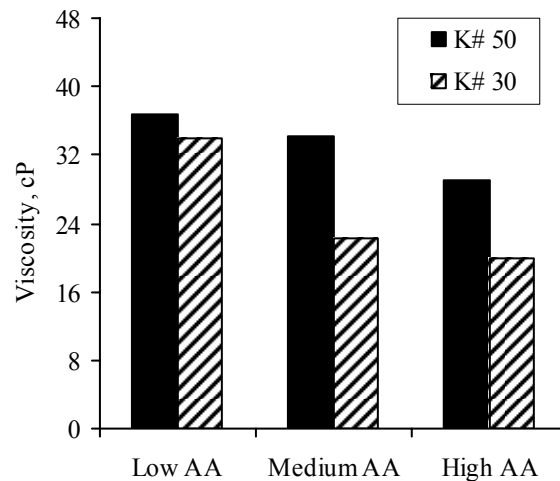
Figure XI.2. Pulp viscosity for low, medium, and high AA softwood kraft pulps.

Hardwood kraft pulping studies were carried out in a similar manner to obtain pulps with a conventional kappa number of 20 and a high kappa number of 26, employing different H-factors and active alkali charges as indicated in Table XI.2. Figures XI.3 and 4 summarize the pulp yield and viscosity results for these kraft cooks. For the conventional kappa 20 pulps, higher alkali charge pulping resulted in lower yield and lower viscosity than the pulps prepared with the lower alkali charge. Low AA pulping provided a ~2% improvements in pulp yield and ~13 cP gain in viscosity in comparison to high AA pulping for conventional kappa 20 pulp. For the high kappa 26 pulp, low AA pulping resulted in only slightly higher yield in comparison to high AA pulping, however, a significant improvement of ~13 cP in viscosity was observed. The results indicate that hardwood kraft pulping, with a low alkali charge, provides better pulping selectivity than high alkali charge in a manner analogous to the softwood kraft pulping results.

Figure XI.3. Pulping yield for low, medium and high AA hardwood kraft cooking.

Figure XI.4. Pulp viscosity for low, medium and high AA hardwood kraft pulps.

## Influence of Pulping Conditions on Oxygen Delignification

Oxygen Delignification Bleachability

Softwood low AA, medium AA and high AA kraft pulps with a conventional kappa number of 30 were O-delignified employing the following conditions: NaOH 1 - 5%, temperature 70-110° C, O_2 pressure 40 psig, medium consistency 10%, and reaction time of 60 min. Figures XI.5 and 6 summarize the relationship of kappa reduction versus NaOH charge and temperature for the oxygen delignification of kappa 30 softwood pulps produced under different pulping conditions. The single stage oxygen studies demonstrate that the differences in pulping technology have a distinct effect on the performance of the O-stages. Figures X
I. 5 and 6 show that high AA pulp had a lower post O stage kappa numbers in comparison to low AA pulp when employing the same temperature and caustics charges. This result indicates that the softwood kraft pulps produced with low AA were slightly more difficult to delignify using oxygen as compared to the high AA pulps. The results demonstrate that the high AA softwood kraft pulp exhibits an improved O-delignification response.

Hardwood low AA, medium AA and high AA pulps with a conventional kappa number of 20 were also O-delignified employing the following conditions: NaOH 1 – 4.5%, temperature 70-110 °C, O_2 pressure 40 psig, medium consistency 10%, and reaction time 60 min. Figures XI.7 and 8 summarize the relationship of kappa reduction versus NaOH charge and reaction temperature for the oxygen delignification of kappa 20 hardwood kraft pulps. At a constant O-delignification temperature, an increase in NaOH charge resulted in an increased kappa number reduction for all the pulps. At a constant NaOH charge, a higher oxygen delignification temperature also resulted in greater lignin removal. In general, oxygen delignification of the kraft pulp produced with the higher

AA resulted in greater delignification. These results clearly indicated that for the hardwood kraft brownstocks high AA pulping yields an improvement with respect to oxygen delignification.
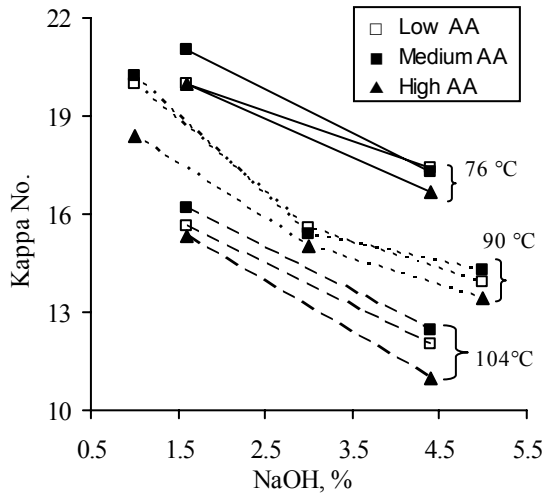
Figure XI.5. Pulp kappa number versus caustic charge O-delignified SW kappa 30 kraft pulp.
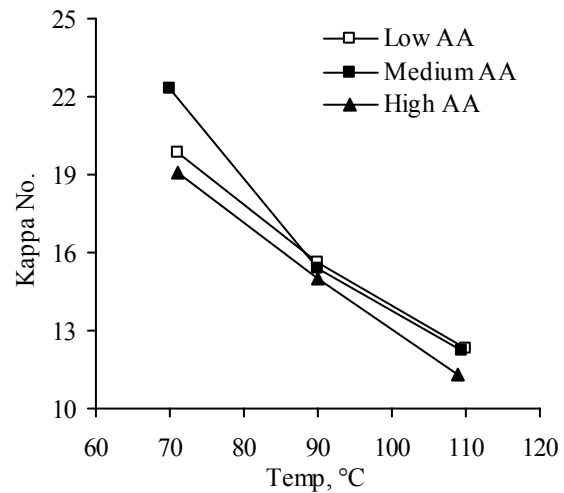
Figure XI.6. Pulp kappa number versus temp. for for O- delignification SW kappa 30 kraft pulp employing 3% NaOH charge.
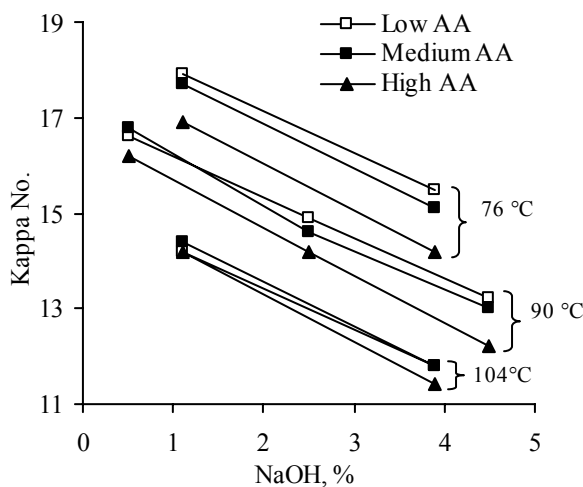
Figure XI.7. Pulp kappa number versus caustic charge for O-delignified hardwood kappa 20 kraft pulp.

Figure XI.8. Pulp kappa number versus temp. for O- delignification hardwood kappa 20 kraft pulp.

Oxygen Delignification Selectivity

Figures XI. 9 and 10 present the yield and pulp viscosity versus the kappa number

relationships for the oxygen delignified softwood kraft brownstocks having an initial kappa number of 30. Figures XI.11 and 12 summarize the same results for the o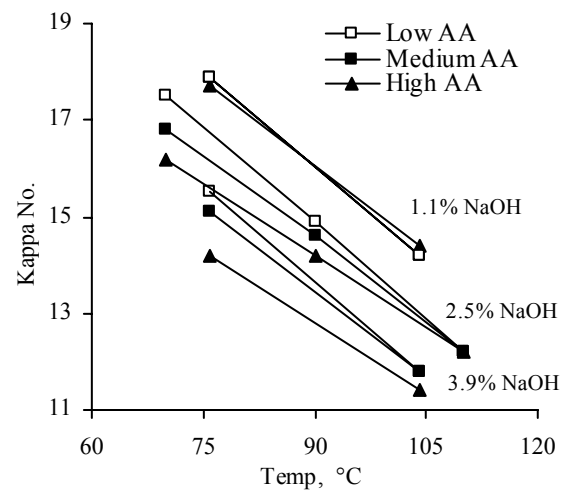xygen delignified hardwood kraft brownstocks having an initial kappa number of 20. These results clearly demonstrate that kraft pulps produced with different pulping protocols exhibit different responses towards oxygen delignification.

Oxygen delignification of the softwood kraft brownstocks prepared in this study resulted in the medium AA kraft pulp exhibiting a higher yield than low AA pulp and high AA pulp after oxygen delignification, whereas, its viscosity is lower than low AA pulp. Low AA pulps had improved yield and viscosity responses than high AA pulp, indicating that low AA pulp resulted in higher oxygen delignification selectivity in term of the yield and viscosity. The low AA softwood kappa 30 pulp provided, on average, yield improvements of 2% and 4 cP in viscosity over the high AA pulp for the oxygen delignification. Similar results were observed for hardwood kappa 20 kraft brownstock pulps. The average oxygen delignification yields observed in this study exhibited the following trend: Low AA pulp > medium AA pulp> high AA pulp (see Figure XI.11). Low AA hardwood pulp had an average improvement of ~ 4% in yield with respect to the high AA kraft brownstocks after oxygen delignification. Figure XI.12 showed that low AA hardwood pulp had a higher pulp viscosity after oxygen delignification than high AA and medium AA pulp. The low AA hardwood kraft pulp had an improvements of 6~12 cP in viscosity than high AA hardwood pulp.
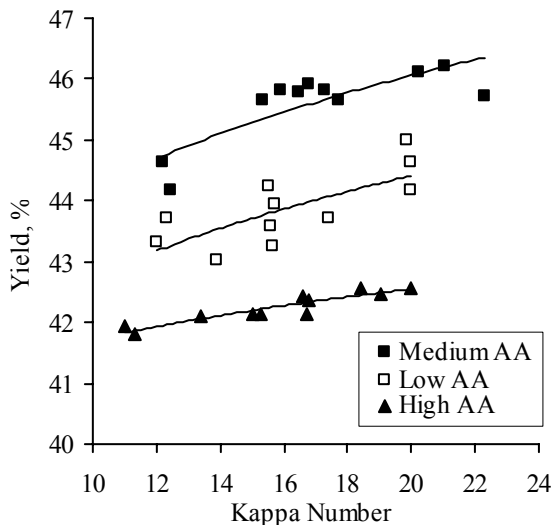
Figure XI.9. Yield versus kappa during O- delignification of SW kraft pulps with kappa 30.
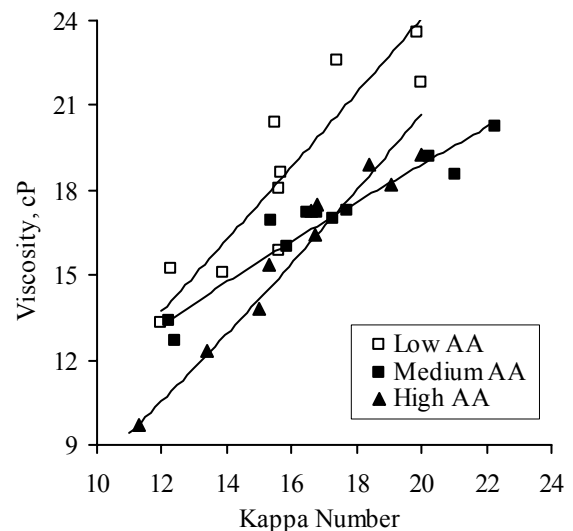
Figure XI.10. Viscosity versus kappa # en during O-delignification of SW kraft pulp with kappa 30.
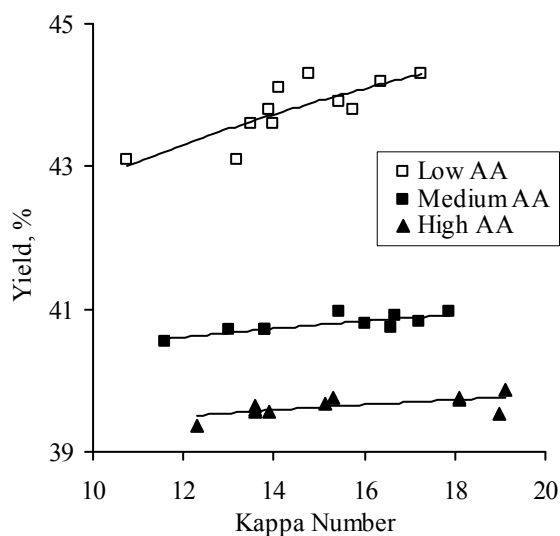
Figure XI.11. Yield versus kappa during O-delignification of HW kraft pulps with kappa 20.
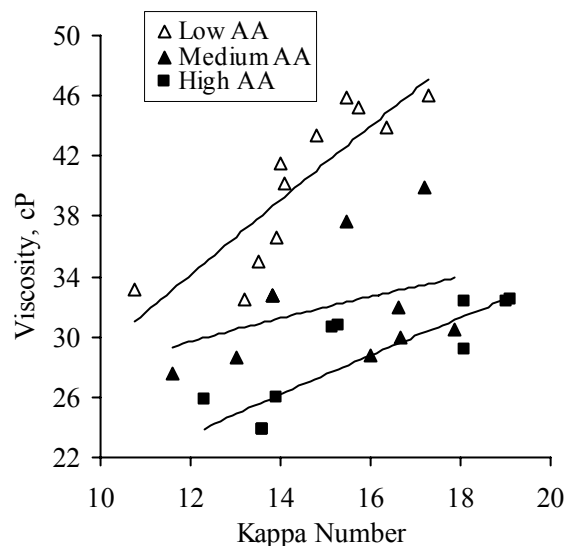
Figure XI.12. Viscosity versus kappa # during O-delignification of HW kraft pulp with kappa 20.

Effects of Temperature and Caustic Charge on Oxygen Delignification

In order to investigate the effects of temperature and caustic charge on oxygen delignification, the low AA softwood kraft brownstock pulp (kappa 30) was subjected to single stage oxygen delignification at different temperatures and caustic charges. Figures XI. 13 and 14 summarize the relationship of kappa number and NaOH charge and reaction temperature on the oxygen delignification process. Higher caustic charge and temperature resulted in more lignin removal during the oxygen delignification. For the O-stages performed at 76°C, an increase of caustic charge from 1.6% to 4.4% resulted in 2.6 kappa reduction (see Figure XI.13), while an increase of caustic charge from 1.6% to 3.0% resulted in 4.4 kappa number reduction at temperature 90 °C. This demonstrated that increase of caustic charge had very small impact to facilitate lignin removal when oxygen delignification was carried out at low temperature of 76 °C. Likewise, at lower caustic charge, temperature increase has lower amount of lignin removal than at higher caustic charge (see Figure XI.14).
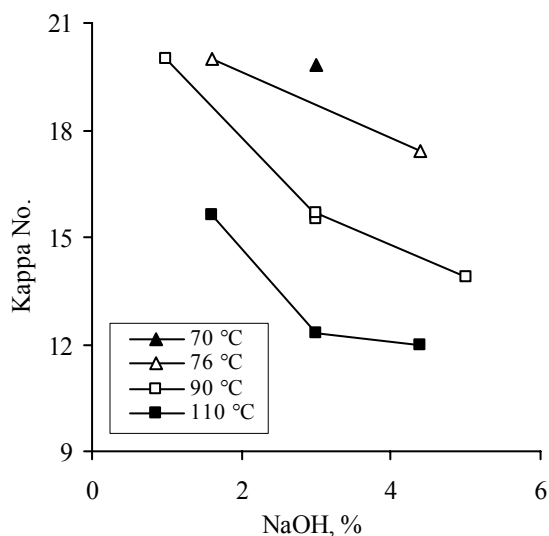
Figure XI.13. Kappa number versus NaOH charge during O-delignification of SW pulps with kappa # 30 pulp.
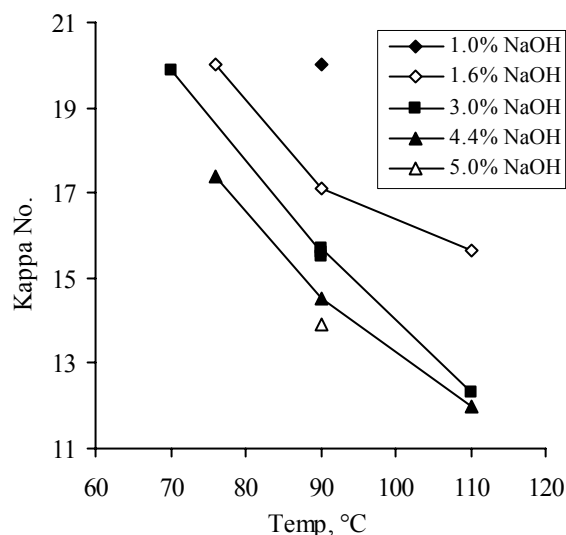
Figure XI.14. Kappa number versus temperature O-delignification of SW pulps with kappa # 30 Pulp.

Influences of High Kappa Pulping on Oxygen Delignification

High kappa softwood pulps were prepared with different pulping technologies, followed by oxygen delignification. Figure 15 shows the relationship of kappa versus NaOH charge for the first stage oxygen delignification of softwood kappa 50 pulps at temperature of 90 °C. It can be seen in Figure XI.15 that low AA pulp has a higher post-O kappa number at the same NaOH charge. Figure XI.16 shows the relationship of kappa versus temperature for the first stage oxygen delignification of softwood kappa 50 pulps at 3.0% NaOH charge. Low AA has a higher post-O kappa lignin content at the same temperature. These results indicate that high AA pulping also results in higher oxygen bleachability for the softwood high kappa pulp.

Figures XI.17 and 18 show the yield and pulp viscosity versus the kappa number relationships for the first stage oxygen delignified softwood high kappa pulps (k# 50). The average first stage oxygen delignification yield is as follows: Low AA pulp > medium AA pulp> high AA pulp (see Figure XI.17). The average pulp viscosity is as follows: Medium AA pulp > low AA pulp > high AA pulp (see Figure XI.18). The low AA pulp has an average improvement of ~3% in yield and an average improvement of 3 cP in viscosity over the high AA pulp during the first oxygen delignification. The results clearly demonstrate different pulping technology produces pulp with different response to the oxygen treatment. High kappa pulp from high AA pulping had lower selectivity of oxygen delignification than that from low AA pulping.
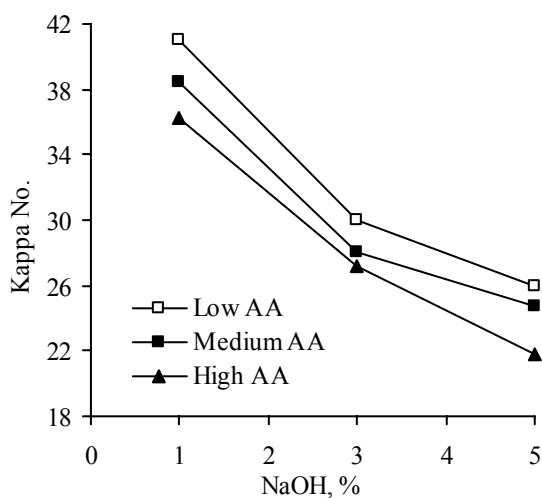
Figure XI. 15. Pulp kappa number versus caustic charge for O- delignified SW high kappa pulp (k# 50) at temperature 90° C.
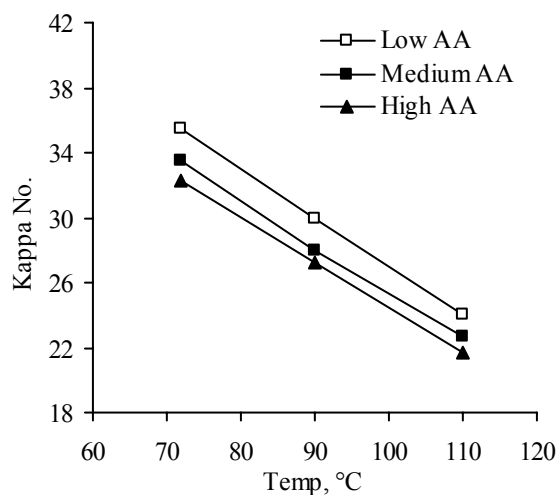
**Figure XI.16.** Pulp kappa # versus temp. for O- delignification SW high kappa pulp (k# 50) at 3% NaOH charge.
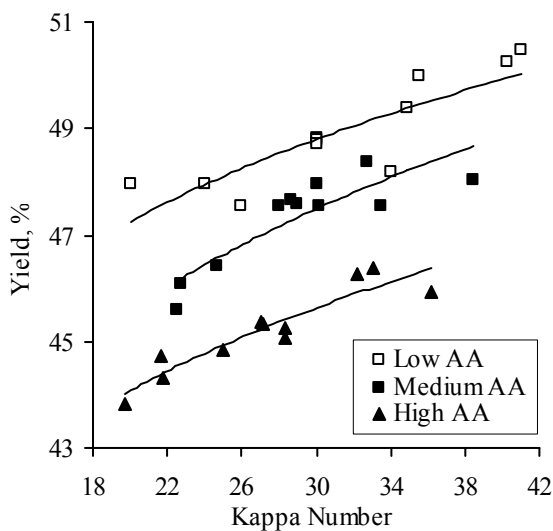

Figure XI.17. Yield versus kappa during O-delignification of SW high kappa pulp (k# 50).
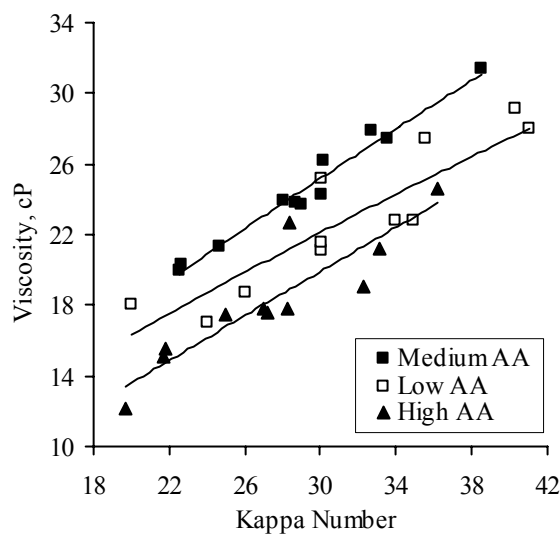
Figure XI.18. Viscosity versus kappa during O-delignification of SW high kappa pulp (k# 50).

Modeling Studies

The results of the SW studies indicate that the differences in pulping technology have a distinct benefit on the performance of the OO-stages. The results of the OO-treatment, under the conditions employed, indicated that the LAA pulp provided improved yield performance. In contrast, the HAA pulp exhibited an improved O-delignification

response. This data were analyzed employing standard SAS analysis and this yielded mathematical relationships for the kappa, yield, and viscosity of the oxygen delignified pulps, these relationship were readily analyzed and modeled, as described below:

SAS Models for O-delignification OF Low Kappa 30 SW Kraft Pulp
Low AA (17%) Kraft Brownstock
- KAPPA= 15.77 – 2.636*((NaOH –3)/2)– 3.652*((Temp-90)/20) + 1.112*((NaOH-3)/2)2
- YIELD= 44.06 – 0.444 *((NaOH –3)/2)– 0.646 *((Temp-90)/20) – 0.5525*((NaOH-3)/2)2
- VISCOSITY= 19.154 –2.788 *((NaOH –3)/2)– 5.686 *((Temp-90)/20)

Medium AA (19%) Kraft Brownstock
- KAPPA= 15.484 –2.577*((NaOH –3)/2)– 4.0 *((Temp –90)/20) + 1.3317*((NaOH-3)/2)2
- YIELD= 43.25 –0.411 *((NaOH –3)/2)– 0.65 *((Temp-90)/20) –0.561 *((NaOH –3)/2)*((Temp-90)/20) – 0.723*((TEMP-90)/20)2
- VISCOSITY= 16.89 –1.904 *((NaOH –3)/2)– 2.732 *((Temp-90)/20)

High AA (21%) Kraft Brownstock
- KAPPA= 15.323 – 2.606*((NaOH –3)/2)– 3.78*((Temp-90)/20) + 0.137*((NaOH-3)/2)2
- YIELD= 41.3059 – 2.0 *((NaOH –3)/2)– 0.3005 *((Temp-90)/20) – 0.1909*((Temp-90)/20)2
- VISCOSITY= 15.245 – 3.328 *((NaOH –3)/2)– 4.162*((Temp-90)/20)

SAS Models for O-delignification of High Kappa 50 SW Kraft Pulp
Low AA (15%) Kraft Brownstock
- KAPPA= 30.112 – 7.065*((NaOH-3)/2) – 6.775*((Temp-90)/20) + 3.706*((NaOH-3)/2)2
- YIELD= 48.906 – 0.914*((NaOH-3)/2)–1.1175*((Temp-90)/2)
- VISCOSITY= 21.842 – 4.673*((NaOH-3)2) – 4.673*((Temp-90)/20) + 1.739*((NaOH-3)/2)2

Medium AA (17%) Kraft Brownstock
- KAPPA= 28.001 –5.316*((NaOH-3)/2) – 3.998*((Temp-90)/2) + 3.147*((NaOH-3)/2)2
- YIELD= 47.298 – 0.800*((NaOH-3)/2) – 0.848*((Temp-90)/20) – 0.659*((Temp-90)/2)*((NaOH-3)/2)
- VISCOSITY= 23.635 –4.287*((NaOH-3)/2)–2.552*((Temp-90)/20) + 2.551*((NaOH-3)/2)2

High AA (19%) Kraft Brownstock
- KAPPA= 26.467 –5.716*((NaOH-3)/2) – 4.975*((Temp-90)/20) – 2.390*((NaOH-3)/2)2
- YIELD= 45.215 –0.776*((NaOH-3)/2) – 0.858*((Temp-90)/20

- VISCOSITY= 17.33 – 4.618*((NaOH-3)/2) –1.735*((Temp-90)/20) – 2.651*((NaOH-3)/2)2

The results from the oxygen bleaching of low HW kappa kraft pulp shows that pulping at a higher active alkali charge increased the bleaching efficiency of oxygen bleaching. This means that a lower kappa number could be achieved at similar oxygen bleaching conditions. Increasing the %AA from 14 to 18%, decreased the kappa number slightly. But the yields for the low active alkali pulps were significantly higher than that for the high active alkali pulps. Single stage oxygen bleachability of these pulps has been completed as a function of caustic charge and temperature. The following models were developed for the conditions studied.

SAS Models for O-delignification of Kappa 19 HW Kraft Pulp
Low AA (14%AA)
- KAPPA =14.8-1.53*NAOH-2.84*TEMP+0.4*NAOH2
- VISCOSITY =40.3-4.68*NAOH-4.69*TEMP
- YIELD= 43.8 -0.35354*NAOH - 0.51515*TEMP

Medium AA (16%AA)
- KAPPA=14.41-1.38*NAOH-2.54*TEMP+.97*NAOH2
- YIELD = 40.54-.01*NAOH-.06*TEMP+.124*TEMP2+.27*NAOH2
- VISCOSITY= 31.39129+0.62753*NAOH+2.32143*NAOH*TEMP-2.77632*TEMP2

High AA (18%AA)
- KAPPA =14.2-2.0*NAOH-1.98*TEMP
- YIELD =98.81956-0.28535*NAOH-0.19444*TEMP+0.42546*NAOH2
- VISCOSITY= 31.39129+0.62753*NAOH+2.32143*NAOH*TEMP-2.77632*TEMP2

Chapter VI. Conclusions

The results demonstrate that practical variations in digester control can have a tremendous impact on the oxygen bleachability of conventional kappa and high-kappa softwood kraft pulps, as well as hardwood pulp. Improved physical pulp properties and yield can be delivered by controlling the H-factor and active alkali charge. These process changes have a significant impact on pulp oxygen delignification bleachability and selectivity. Low AA softwood kappa #30 pulp has an average improvement of 2% in yield and 4 cP in viscosity in comparison to high AA pulp for the oxygen delignification, as well as an average improvement of ~3% in yield and 3 cP in viscosity for low AA high kappa #50 pulp. Low AA hardwood kappa #20 pulp had an average improvement of ~4% in yield and 6~12 cP in viscosity compared to high AA pulp.

Chapter VI. References

1. Magnotta, V.; Kirkman, A.; Jameel, H.; Gratzl, J. High-kappa pulping and extended oxygen delignification to increase yield.   Breaking the Pulp Yield Barrier Symposium, Atlanta, 165-182 (Feb., 1998).

Chapter XII. Improving HW Bleached Kraft Pulp Production via Integrated Kraft pulping and O-Delignification Technologies

Our prior studies into extended oxygen delignification indicated that for HW kraft pulps that oxygen bleachability of conventional kappa and high-kappa pulps was improved by carefully controlling the H-factor and active alkali charge of the cook. These process changes have a significant impact on pulp oxygen delignification bleachability and selectivity. Low AA hardwood kraft pulps with a kappa number of 20 pulp had an average improvement of ~4% in yield and 6~12 cP in viscosity compared to high AA pulp. Although some benefits were observed for controlling active alkali/H-factor of high kappa HW kraft pulps, our previous studies were compounded with high levels of rejects. This chapter examines promising methods of addressing this latter issue.

Chapter XII. Experimental

Materials

Hardwood Kraft Pulps. Screened hardwood chips were obtained from a commercial U.S. kraft pulp mill. All kraft cooks were performed in an M&K digester at several alkali charges and H-factors keeping sulfidity constant at 25%, see Tables XII.1, 2, 5, and 6 for further technical details.

Oxygen Delignification. One and two-stage oxygen delignification experiments were conducted using a rotating bomb reactor. In a typical oxygen delignification experiment, the reactor was charged with 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 (2.5%). After sealing the reactor, the vessel was pressurized with O_2 (40 psi) and heated to 90 ^{o}C for a single O-stage and 104°C for OwO treatment. The reaction was terminated after 1 h, the reactor was cooled, and the O_2 pressure was released. The pulps were then washed, dried, and analyzed for pulp properties. For the OO stage experiments, the pulp was washed with deionized water between the first and second stage, charged with bleaching chemicals and treated to a second O-stage. The results of these studies are summarized in Tables XII.3, 4 and 7-10.

Pulp Analyses. Kappa number was measured according to TAPPI Method um-246. Typical experimental standard deviations for this procedure were determined to be ±0.5% for the high kappa pulps.

Chapter XII. Results and Discussion

A key concern when proposing to manufacture high kappa hardwood kraft pulps is the higher amount of rejects generated.[1] Reduction of the rejects is possible if the rejects are sent to the oxygen delignification stages and screening is done after the first oxygen

delignification stage. Another alternative is to understand the factors contributing to high reject rates for hardwood kraft pulps. If the rejects cannot be decreased with increasing kappa number, most of the benefits of high kappa pulping of hardwood are negatively impacted.

To study this phenomena, research efforts were directed at evaluating the impact of pulping temperature on rejects for both low (kappa # 19) and high lignin content HW kraft pulps (kappa # 25). The results for the low kappa HW kraft pulping studies are summarized in Tables 1 and 2. Decreasing the pulping temperature from 170 to 160 ^{o}C, provided a small reduction in the reject rate. There was also a small beneficial effect on the total yield. The biggest impact on the yield was shown to be caused by a decrease in the %AA. The response of the pulps at both temperatures to oxygen bleaching was also measured. These results are shown in Tables 3 and 4. All the pulps were oxygen bleached at a constant oxygen delignification condition (2.5% NaOH, 90°C, 60 min). The pulps from 160 ^{o}C, had equivalent bleaching response, but the rejects after oxygen bleaching were lower for the 160 ^{o}C pulps with respect to comparable experiments performed on the kraft pulps cooked at 170 ^{o}C.

Table XII.1. Kraft Pulping[a] of Hardwood Employing Cooking Temperature 160 ^{o}C to 19 Kappa.

Active Alkali (AA)	H Factor	Kappa #	Total Yield, %	Rejects, %
Low AA: 14%	1050	19.0	50.2	0.70
Medium AA: 16%	650	18.5	48.4	0.90
High AA: 18%	500	19.0	47.4	1.40

[a]sulfidity 25%, liquor/wood 4:1.

Table XII.2. Kraft Pulping[a] of Hardwood Employing a Cooking Temperature of 170 ^{o}C to 19 Kappa.

Active Alkali (AA)	H Factor	Kappa #	Total Yield, %	Rejects, %
Low AA: 14%	1000	19.6	50.0	1.0
Medium AA: 16%	650	19.3	48.2	1.1
High AA: 18%	500	19.9	47.3	1.5

[a]sulfidity 25%, liquor/wood 4:1.

Table XII.3. Oxygen Delignification[a] of 19 Kappa HW Kraft Pulps
(Kraft Cooking Temp:160 ^{o}C)

Active Alkali (AA)	Kappa #	Rejects, %	Screen Yield, %	Overall Yield, %
Low AA: 14%	14.6	0.5	90.1	45.5
Medium AA: 16%	14.2	0.7	91.2	44.5
High AA: 18%	14	1.0	92.1	44.0

[a]Single Oxygen Stage Conditions: %NaOH=2.5%, Time = 60 min, Temp= 90°C

Table XII.4. Oxygen Delignification[a] of 19 Kappa HW Kraft Pulps (Kraft Cooking Temp: 170 °C)

Active Alkali (AA)	Kappa	Rejects, %	Screen Yield, %	Overall Yield, %
Low AA: 14%	14.9	0.4	89.0	44.7
Medium AA: 16%	14.6	0.6	90.0	43.7
High AA: 18%	14.2	--	91.2	43.8

[a]Single Oxygen Stage Conditions: %NaOH=2.5%, Time = 60 min, Temp= 90°C

The results of the pulping for the high kappa hardwood kraft pulps are shown in Table 5 and 6. At the lower cooking temperatures pulp yields were significantly higher than when employing higher pulping temperatures. In addition, there was also a significant improvement in the reject rate. At the mid AA level, the rejects decreased from 5.5% to 4.2%.

Table XII.5. Kraft Pulping[a] of Hardwood Employing Cooking Temperature 160 °C to 25 Kappa.

Active Alkali (AA)	H Factor	Kappa #	Total Yield, %	Rejects, %
Low AA: 12%	2500	25.0	52.4	3.0
Medium AA: 14%	900	25.0	51.9	4.2
High AA: 16%	550	26.0	51.8	5.2

[a]sulfidity 25%, liquor/wood 4:1.

Table XII.6. Kraft Pulping[a] of Hardwood Employing a Cooking Temperature of 170 °C to ca. 25 Kappa.

Active Alkali (AA)	H Factor	Kappa #	Total Yield,%	Rejects, %
Low AA: 12%	3600	26.8	50.0	4.9
Medium AA: 14%	900	24.2	49.7	5.5
High AA: 16%	550	26.5	49.6	5.8

[a]sulfidity 25%, liquor/wood 4:1.

The pulps described in Tables 5 and 6 were subsequently oxygen bleached employing an OwO treatment without any rejects removal prior to first stage oxygen bleaching. After the initial O-stage, remaining rejects were removed and the remaining pulp was sent to the second oxygen bleaching stage. The results for these studies are summarized in Tables 7 - 10. The delignification response to the oxygen bleaching stages for the HW kraft pulps prepared at cooking temperatures of 160 and 170 °C were comparable, but the rejects after the first oxygen stage was significantly lower. The overall yields for the high kappa pulps were significantly higher when pulping was done at 160°C as compared to 170°C. The yields were almost 2% higher for all the cases.

Table XII.7. First Stage of OwO Delignification[a] of High Kappa HW Kraft Pulps Prepared at 160 °C

Active Alkali (AA)	Kappa #	Rejects, %	Screen Yield, %	Overall Yield, %
Low AA: 12%	16.1	1.4	91.1	47.2
Medium AA: 14%	15.8	2.8	90.8	45.8
High AA: 16%	15.2	3.6	91.0	44.5

[a]Single Oxygen Stage Conditions: %NaOH=2.5%, Time = 60 min, Temp= 104 °C

Table XII.8. First Stage of OwO Delignification[a] of High Kappa HW Kraft Pulps Prepared at 170 °C

Active Alkali (AA)	Kappa	Rejects, %	Screen Yield, %	Overall Yield, %
Low AA: 12%	16.0	3.1	91.4	44.2
Medium AA: 14%	15.8	3.8	90.3	43.0
High AA: 16%	15.3	4.5	90.4	42.6

[a]Single Oxygen Stage Conditions: %NaOH=2.5%, Time = 60 min, Temp= 104 °C

Table XII.9. Second Stage of OwO Oxygen Delignification[a] of High Kappa HW Kraft Pulps Prepared at 160 °C

Active Alkali (AA)	Kappa #	Rejects, %	Screen Yield, %	Overall Yield, %
Low AA: 12%	10.6	-	97.1	45.8
Medium AA: 14%	11.8	-	98.6	45.2
High AA: 16%	11.7	-	99.0	44.1

[a]Single Oxygen Stage Conditions: %NaOH=2.5%, Time = 60 min, Temp= 104 °C

Table XII.10. Second Stage of OwO Oxygen Delignification[a] of High Kappa HW Kraft Pulps Prepared at 170 °C

Active Alkali (AA)	Kappa	Rejects, %	Screen Yield, %	Overall Yield, %
Low AA: 12%	11.0	-	98.6	43.6
Medium AA: 14%	12.1	-	98.9	42.5
High AA: 16%	12.0	-	99.0	42.2

[a]Single Oxygen Stage Conditions: %NaOH=2.5%, Time = 60 min, Temp= 104 °C

Chapter XII. Conclusions

In summary, the lower kraft cooking temperature in combination with the medium AA shows great promise for integrating high kappa pulping of hardwoods with an advanced extended oxygen delignification stage. Thereby providing a practical means of improving HW kraft pulping and bleaching operations with minimal capital requirements for a pulp mill, while improving pulp quality and operating profitability.

Chapter XII. References

[1]. Kopanidis, J. "Improved kraft pulping of eastern hardwoods for bleached paper grades. Laboratory study, economic analysis, and implementation" Tappi J., 60(2), 79(1977).

Chapter XIII. Pulp Properties of Low and High Kappa Kraft Pulps O-Delignified and Bleached D(E+P+O)D

The results of this program have clearly demonstrated that kraft pulping and oxygen delignification need to be considered on a "system approach" to maximize pulp production and physical strength properties. Furthermore, we have clearly demonstrated that a higher proportion of delignification should be shifted to oxygen delignification stage(s) by cooking the pulp to a higher kappa number for both hardwood and softwood kraft pulps. Oxygen delignification is more selective than the kraft cooking process and provides pulps with enhanced physical properties and pulp yields. These benefits can be maximized by controlling active alkali and H-factor, which can be readily integrated into modeling systems as reported in earlier chapters. The higher pulp yield can translate into a lower organic load to the recovery boiler, and for recovery–limited mills an increase in capacity can be achieved. A strong environmental incentive to use oxygen delignification is that it is chlorine–free and effluents are compatible with mill closure.

The need to investigate the final pulp properties of fully bleached kraft pulps from low and high-kappa kraft pulps is one of the concluding objectives of this program. This was accomplished by bleaching a series O and OO kraft pulps via the sequence D(E+P+O)D and characterizing the pulps for optical and physical properties.

Chapter XIII. Experimental

Materials. Low and high kappa SW and HW kraft pulps, prepared in the earlier phases of this study were oxygen delignified (see Chapter 11 and 12) and were utilized for all bleaching studies reported in this chapter.

SW and HW Bleaching Conditions. Chlorine dioxide delignification (D_0) stages were preformed at 10% csc, 70 ^{o}C for 60 minutes employing 0.23 kappa factor for SW and 0.21 for HW kraft pulps. The terminal pH of the D-stage was typically between 1.8 – 1.9. and the pulp was then filtered, washed, and used in the subsequent stage. The (E+P+O) stages were preformed at 10% consistency, 70 ^{o}C with a caustic factor for 0.5, a 0.5% charge of H_2O_2 and 35 psi O_2 pressure for a total of 60 min. A terminal pH of 11 was recorded for the (E+P+O) stage and the resulting pulps P number of 2.3 and ISO brightness values were ~81. The final chlorine dioxide brightening stage (0.4% charge) was conducted at 10% consistency in polyester bags at 70 ^{o}C for 180 minutes with a terminal pH of 3 - 4. The resulting pulp was washed and handsheets were prepared for optical and physical testing according to standard TAPPI testing protocols.

Refining Studies. All kraft pulps were PFI refined with 1000 - 7000 revs and physical pulp properties including zero span tensile, tensile, burst, and tensile index, were determined according to standard TAPPI methods.

Chapter XIII. Results and Discussion

FQA analysis of select SW O-delignified and D(E+P+O)D pulps are summarized in Table XIII.1 and this data indicates that the basic fiber properties of the high kappa kraft pulp are comparable to the low kappa pulp after O stage and ECF bleaching.

Table XIII.1 Fiber properties of O, OO, and ECF treated pulps as analyzed by FQA.

Pulp	Percentage Fine, %*	Mean Length*, mm	Mean Curl Index*	Mean Kink Index, 1/mm
30-O	0.37	2.67	0.16	1.32
50-OO	0.33	2.67	0.14	1.31
30-O D(E+P+O)D	0.28	2.50	0.20	1.86
50-OO (E+P+D)D	0.35	2.42	0.23	1.92

*: Length weighted.

Table XIII.2 Physical strength properties of O, OO, and D(EPO)D SW kraft bleached pulps.

Pulp Sample (brownstock kappa #)	PFI Rev.	Freeness	Tear index mN.m²/g	Tensile Index N.m./g	Burst Index kPa.m²/g	Zero-Span N.m./g
LAA 30-O	0	780	19.9	24.9	1.38	132.8
	1000	710	17.3	56.3	4.16	132.5
	3000	544	15.3	63.4	4.94	137.7
	6000	216	11.0	91.0	6.75	143.8
	7000	94	10.2	102.4	7.06	151.2
LAA 30-O D(EPO)D	0	758	19.4	20.9	1.00	119.6
	1000	684	14.4	58.7	4.17	129.7
	3000	386	10.6	79.6	5.15	139.4
	6000	104	9.0	87.7	7.25	136.7
HAA 30-O D(EPO)D	0	748	21.9	29.9	1.82	130.0
	1000	691	17.7	48.3	3.69	134.4
	3000	416	12.3	72.7	5.07	138.9
	6000	126	9.8	87.7	6.54	141.4
LAA 50-O(30)O *	0	744	21.3	33.2	2.03	127.8
	1000	677	12.5	60.6	4.34	136.1
	3000	432	9.3	80.3	6.00	140.0
	6000	173	8.2	84.2	6.77	144.5
LAA 50-	0	751	20.8	28.9	1.73	120.6
	1000	663	13.0	57.5	4.43	128.6

O(30)O* D(EPO)D	3000	365	10.0	76.7	6.28	139.3
	6000	111	9.3	77.7	6.53	140.8
HAA 50-O(30)O	0	745	20.8	35.4	2.18	120.4
	1000	677	13.1	63.3	4.81	140.3
	3000	412	9.7	83.7	6.26	145.4
	6000	160	8.4	86.6	6.75	149.3
HAA 30-O	0	752	19.0	21.0	0.97	131.5
	1000	716	18.9	57.3	3.71	149.4
	3000	527	13.7	82.7	5.67	154.2
	6000	263	12.2	80.8	6.17	157.2
HAA 50-O(30)O D(Eop)D	0	738	13.4	16.1	0.64	107.9
	1000	679	14.0	55.0	3.89	137.1
	3000	428	9.9	75.2	5.50	146.9
	6000	204	9.3	77.9	5.81	145.6
LAA 50-O(30)O**	0	746	18.6	26.5	1.33	126.7
	1000	685	11.8	65.5	4.51	144.7
	3000	472	9.1	81.0	5.87	148.3
	6000	231	8.9	84.2	6.27	156.1
LAA 50-O(30)O** D(Eop)D	0	739	15.6	15.9	0.84	106.9
	1000	667	13.2	60.0	4.32	139.4
	3000	385	9.5	81.0	6.06	142.6
	6000	190	8.8	84.1	6.17	148.6

LAA: Kraft brownstock prepared via Low active alkali conditions; HAA: kraft brownstock prepared via High active alkali; *: 3.0% alkali charge for the second O_2 stage; **: 1.6% alkali charge for the second O_2 stage (see chapter XI for further pulping/O-delignification conditions). Final Brightness ISO Brightness 88% .

Table XIII.2 summarizes the beating and physical strength properties of O, OO, and ECF treated pulps. At the same beating revolution, high kappa OO and ECF treated pulps have lower freeness. High kappa OO treated pulps are found to have improved beating properties in comparison to the low kappa O treated pulp. High kappa OO pulp shows higher tensile, burst, and zero-span strength, and lower tear strength than low kappa O pulp at a comparable beating revolution. This further indicates that high kappa OO pulp exhibits improved strength properties upon beating. After ECF bleaching, pulp shows lower zero-span value, which is attributed to the higher amounts of curl and kink. In our earlier studies we had shown that the zero-span strength decreased steadily with an increased O delignification when employing higher bleaching temperatures and alkaline charges. Since high kappa and low kappa pulps were delignified to the same delignification degree after O or OO stage, they were found to exhibit comparable zero-span properties. Both high kappa OO and low kappa O treated pulp are suitable for ECF bleaching to get acceptable strength properties.

Table XIII.3 presents the results of D(EPO)D bleaching of a series of low and high kappa HW kraft pulps prepared in chapter 12 bleached to a common ISO brightness value of 84. Although some differences were apparent between the low and high kappa pulps, overall

the pulps had very comparable physical strength properties suggesting that it is possible to capture the benefits of halting a kraft cook early and removing the extra lignin by an extended O-delignification process.

Table XIII.3 Physical strength properties of OD(EPO)D HW kraft bleached pulps.

HW Kraft OD(EPO)D (brownstock kappa #)	PFI Rev.	Tensile Index N.m./g	Burst Index kPa.m^2/g	Tear index mN.m^2/g
Low-Kappa Pulps				
LAA(20):170 ^{o}C	3000	71.0	4.3	11.0
	5000	76.2	4.9	10.8
MAA(20)):170 ^{o}C	3000	73.0	4.6	11.1
	5000	78.8	5.0	10.6
HAA(20)):170 ^{o}C	3000	70.8	4.4	10.2
	5000	73.9	4.9	9.9
LAA(19):160 ^{o}C	3000	88.4	6.2	10.8
	5000	89.3	6.4	10.4
MAA(19):160 ^{o}C	3000	80.5	5.5	11.1
	5000	87.2	6.1	11.0
HAA(19):160 ^{o}C	3000	75.2	4.8	9.4
	5000	77.3	5.1	9.3
High-Kappa Pulps				
LAA(27):170 ^{o}C	3000	75.9	4.9	11.4
	5000	79.0	5.3	11.3
MAA(24):170 ^{o}C	3000	70.7	4.5	10.8
	5000	79.7	5.4	10.2
HAA(27):170 ^{o}C	3000	69.3	4.4	12.0
	5000	80.8	5.4	11.3
LAA(20):160 ^{o}C	3000	75.1	4.9	9.9
	5000	80.5	5.6	9.7
MAA(20):160 ^{o}C	3000	79.2	5.1	10.2
	5000	87.1	5.8	10.0
HAA(20):160 ^{o}C	3000	75.0	4.7	8.4
	5000	79.9	5.2	8.3

LAA: Kraft brownstock prepared via Low active alkali conditions, see chapter XII for further details; MAA: Kraft brownstock prepared via medium active alkali conditions HAA: kraft brownstock prepared via High active alkali); *: 3.0% alkali charge for the second O$_2$ stage; **: 1.6% alkali charge for the second O$_2$ stage. Final Brightness ISO Brightness 84% .

Chapter XIII. Conclusions

The high kappa kraft pulp show comparable fiber properties after an extended oxygen

delignification and ECF bleaching {D(EPO)D} with low kappa kraft pulps after O stage and ECF bleaching. For the SW pulps our data suggests it is easier to develop the strength properties in high kappa OO pulp upon beating. both high kappa OO and low kappa O treated pulp are suitable for ECF bleaching to get acceptable and comparable strength properties.

Chapter XIV. Overview and Path Forward

This collaborative DOE – industry sponsored had several clear objectives at the beginning of the program including:
- ° Identifying pulping conditions that optimize O and OO performance;
- ° Identifying structural features of lignin that enhance reactivity towards EOD of high kappa pulps;
- ° Identifying factors minimizing carbohydrate degradation and improve pulp strength of EOD high kappa pulps;
- ° Developing a simple, reproducible method of quantifying yield gains from EOD;
- ° Developing process conditions that significantly reduce the capital requirements of EOD while optimizing the yield benefits.

As described in the accompanying chapters, we have fully addressed the program deliverables. Although each chapter highlights key research outcomes it is valuable to highlight the practical implications of these studies, including:

1. The use of a mini-O sequence such as $(E+O)D_{kf:0.05}(E+O)$ or $D_{kf:0.05}(E+O)(E+O)$ without interstage washing could capture approximately 60% of the delignification efficiency of a conventional O-stage without the major capital requirements associated with an O-stage for conventional SW kraft pulps (i.e., kappa # ~ 30).

2. For kappa # ~30 SW kraft pulps O and OO stages exhibited comparable delignification properties, but improved viscosity properties were acquired with the later. The OO-stage for high kappa SW kraft pulps (kappa # ~ 55) exhibited clearly superior delignification and viscosity retention over a single O-stage. Data analysis indicated that high-kappa SW kraft pulps exhibit enhanced O-bleachability over low kappa kraft pulps.

3. Reduced O-bleachability of low-kappa SW kraft pulps is due to increased amounts of condensed phenolics and p-hydroxyphenyl units in the brownstock. These difficult to oxidize lignin units could potentially be minimized by enhanced kraft digester control and plant genetics. In addition, lignin-carbohydrate complexes limit lignin removal during an oxygen-stage and new bleaching catalysts are needed to address this issue.

4. The intrinsic NPE in wood/brownstock have a significant effect on O-delignification selectivity and reactivity. The use of $MgSO_4$ frequently provides distinct benefits for an O-stage, especially for an SW kraft pulps and frequently insignificant for HW kraft pulps. This can be attributed, in part, to the elevated levels of Mg^{2+} present in hardwoods. Optimization of commercial O-stages needs to evaluate Mn and Mg content of incoming wood furnish and then optimize the addition of $MgSO_4$.

5. The effect of efficient mixing speed on oxygen delignification was important, but once an optimal point is determined additional mixing is inconsequential. Mixing was also shown to decrease CFS freeness but have no difference in post-O pulp viscosity.

6. Post-O fiber deformations seemed to correlate well with bleaching temperature and the higher the O-delignification temperature the more the curls and kinks.
7. O-delignification of high kappa HW kraft pulps (i.e., kappa # 29) exhibits significant improvements in terms of O-bleachability and selectivity over low-kappa kraft pulps (i.e., kappa # 11)
8. The content of hexenuronic acids in HW kraft pulps is one of the key components detrimentally impacting O-bleachability of HW kraft pulps. The presence of these acids can be controlled, to some extent, by profiling the kraft cook.
9. The structure of HW lignin influences O-delignification of HW kraft pulps with C5 condensed guaiacyl phenolics and p-hydroxyphenol detrimentally impacting O-bleachability. These parameters can be controlled, to some extent, by profiling the kraft cooking conditions.
10. The rate of formation and loss of fiber charge during an O-stage stage can be employed to maximize net fiber charge. Optimal fiber charge development and optimal delignification are two independent parameters and do not parallel each other. It is possible to utilize an O-stage to enhance overall cellulosic fiber charge of low and high kappa SW kraft pulps which is beneficial for physical strength properties.
11. The application of NIR and multi-variant analysis provides a rapid and simple method of determining the yield of pulp from an oxygen delignification stage that could be rapidly transferred to real-mill applications.
12. Kraft pulping conditions and oxygen delignification of high and low-kappa SW and HW pulps are intimately related. Improved physical pulp properties and yield can be delivered by controlling the H-factor and active alkali charge. Low AA softwood kappa number 30 pulp has an average improvement of 2% in yield and 4 cP in viscosity in comparison to high AA pulp for the oxygen delignification. This differeance is also seen for high-kappa SW kraft pulps with an average improvement of ~3% in yield and 3 cP in viscosity for low AA high kappa #50 pulp. Low AA hardwood kappa #20 pulp had an average improvement of ~4% in yield and 6~12 cP in viscosity as compared to high AA pulp.
13. Lower kraft cooking temperature (160 vs. 170 $^{\circ}$C) in combination with the medium AA provides a practical approach for integrating high kappa pulping of hardwoods (i.e., low rejects) with an advanced extended oxygen delignification stage.
14. ECF pulp bleaching of low and high kappa kraft SW and HW pulps exhibit comparable optical and physical strength properties when bleached D(EPO)D.

Since the initiation of our studies the potential of high-kappa O-delignification of kraft pulps has become a growing issue of importance to the industry. The recent paper by Ragnar highlights the growth of O-delignification systems with Kamyr/Kvaerner alone recently announcing that they have installed 100 systems in which 14 are high consistency systems and 86 are medium consistency systems.[1] Improvements in oxygen delignification, especially two-stage treatments remains a very active field of laboratory and mill-studies.[2,3] Studies by Leroy et al.,[4] have studied fundamental aspects of extended delignification and these studies concluded the role of phenolics limits O-delignification as we have noted in our earlier studies. The role of lignin

reactivity/inactivity pre and post O-delignification was verified in a recent review by Argyropoulos and Lucia.[5]   A recent paper by Martin et al. also highlighted the detrimental limitations of lignin-carbohydrate complexes with concurs with our research conclusions.[6,7] From an industrial prospective our results are supported by a recent paper by Stratton et al. which examined several pulping and bleaching technologies of the 1990s and concluded "The most notable developments have been the widespread adoption of extended and oxygen delignification, the use of modern washing and screening technologies."[8] The values of our modeling studies and demonstrated integration of pulping conditions with O-delignification clearly extends the conclusions Santos[9] presented at the 2000 IPBC conference.

They benefits of extended O-delignification extended beyond the bleaching line. For example, Parsad et al. have reported that stopping a SW kraft cook at kappa 50 followed by more selective OO stages reduces the load on the recovery system including the evaporator, boiler and lime kiln.[10] This paper demonstrated these results are of value for pulp mills working under the constraints of limited digester capacity or limited boiler thermal capacity. Although the performance of an OOD(EPO)D stage in a mill setting was beyond the scope of this program, our results certainly set the stage for pilot-plant and/or mill studies. In Parthasarathy paper, he outlines how the kappa-number-yield relationship suggest that every unit increase in kappa number would contribute approximately 0.19% increase in total brown pulp yield which even after adjusting for screen rejects and yield shrinkage would translate into 1.5 – 3.5% savings in wood consumption to produce a unit of bleached pulp.[11] Our results certainly suggest this is a very viable approach for SW kraft pulps. The initially high-kappa HW kraft oxygen delignification studies in this program indicated that severe reject problems occurred for high-kappa HW kraft pulps, but we demonstrated that this could be managed by reducing the maximum kraft pulping temperature to 160 $^{\circ}$C. Finally, all yield benefits proposed in the study and others proposed technologies needs to be verified by on-line methodologies, which prior to this study was an under examined issues. The discovery of an NIR as a viable approach to this challenge is an exciting technological solution to this challenge.

In summary, this program has presented to its sponsors viable technological solutions to integrating kraft pulping and oxygen delignification into a systems approach to manufacturing bleached kraft pulps. We have identified laboratory pulping parameters that can enhance extended oxygen delignification of SW and HW pulps which can be readily modeled into a predictive program. The resulting pulps were shown to be easily bleached using modern kraft ECF bleaching technologies to yield high-value pulp products. These results should now be extended into pilot-plant and mill-trials.

Chapter XIV. References.

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