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## APPLIED CHEMISTRY

# Chemical Basis for a Selectivity Threshold to the Oxygen Delignification of Kraft Softwood Fiber As Supported by the Use of Chemical Selectivity Agents

Shiyu Fu, Xinsheng Chai, Qingxi Hou, and Lucian A. Lucia\*

*Institute of Paper Science and Technology, Georgia Institute of Technology, 500 10th Street, Northwest, Atlanta, Georgia 30332-0620*

Softwood kraft pulps having different lignin contents ( $\kappa$  numbers) were subjected to alkali oxygen under the application of selectivity enhancing agents, namely,  $\text{MgSO}_4$ , phenol,  $\text{MgSO}_4$ /phenol, and 3-methoxyl hydroxyl quinone, to examine the effect on delignification selectivity. The results demonstrated that there is a synergistic effect between  $\text{MgSO}_4$  and phenol during oxygen delignification. This effect is more obvious for high lignin content pulp than that for low lignin content pulp. Remarkably, examination of the carboxyl groups on pulp fibers and the carbonate content in the effluent liquors demonstrated that the  $\kappa$  number of softwood kraft pulp cannot drop below 7 without incurring cellulose degradation during oxygen delignification despite the application of selectivity enhancement agents.

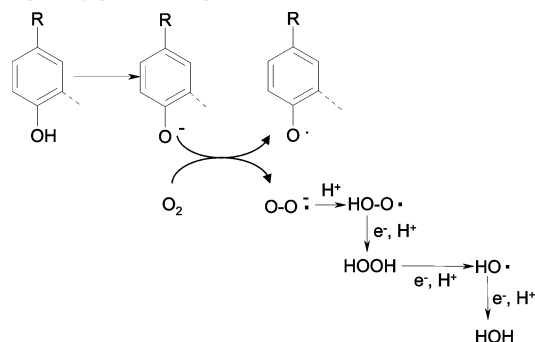
## Introduction

Oxygen delignification (OD) of kraft pulp is currently enjoying widespread use in pulping and bleaching plants as a result of beneficial environmental effects, including its contributions to reductions of AOX (adsorbable organic halides), BOD (biochemical oxygen demand), COD (chemical oxygen demand), and color reduction in the effluent across the bleaching plant. Indeed, it has been shown that it is able to offset total bleaching costs by 20% on average.<sup>1,2</sup> In a typical mill operation, the degree of OD is usually no more than 50% of the original lignin content since forcing the commercial process beyond this level results in severe cellulose depolymerization, causing significant deterioration of important physical properties such as pulp viscosity and fiber strength.<sup>3</sup> Nevertheless, since oxygen is an inexpensive chemical, it is desirable to delignify pulp to lower  $\kappa$  numbers in an OD system. Many efforts have been expended to increase the degree of OD by overcoming the fundamental chemical limitations to the process; for example, Ai<sup>4</sup> reported that both nonionic and anionic surfactants can improve OD without adversely affecting individual fiber breaking length, tear index, burst index, and the folding endurance of the treated pulp; Campion and Suckling found that the demethylation of residual kraft lignin by sodium ethanethiolate could expedite lignin removal during OD presumably as a result of an increase in the levels of phenolate groups which are known to initiate oxidative radical reactions that result in delignification.<sup>5</sup> Both pulp strength and pulp yield, unfortunately, were substantially compromised as a result of the demethy-

lation process, so no further physical testing could be obtained in that study. Recently, the usage of oxidative catalysts for improving the degree of OD under acid conditions has provided favorable results. Evtuguin et al.<sup>6,7</sup> reported that polyoxometalates (POMs) such as the heptamolybdopentavanadophosphate anion can dramatically increase both the degree and selectivity of OD compared to conventional OD. The results of pursuing catalytic OD are promising avenues for future use of OD to improve the efficiency of the modern pulp mill. The main obstacle, however, to successful application of catalysts in typical mill practice are unfavorable economics.

Oxygen delignification is actually based on competitive reactions of oxygen or oxygen-active species within pulp lignin and carbohydrates. In general, lignin removal under alkali-oxygen condition is accompanied by a kinetically less favorable oxidation of carbohydrates, which leads to viscosity drops or, more specifically, a loss in the integrity of the pulp. During the delignification process, the cleavage of etherified  $\beta$ -aryl ether units is well recognized as a significant contribution to lignin removal in the alkaline delignification process,<sup>8</sup> while the cleavage of carbohydrate  $\beta$ -glycosidic bonds contributes to pulp degradation.<sup>9–11</sup> Thus, when the content of lignin in the pulp becomes relatively low (ca.  $\kappa = 10$ ) by increased oxygen delignification, the oxidation of the carbohydrates becomes a more favorable process. *The question thus naturally arises if there exists a lignin content at which the selectivity of oxygen delignification is compromised for maintaining the strongest fiber given the competitive chemistry?* Several have speculated that the minimum outlet  $\kappa$  number for softwood pulp is approximately 14–16 without incurring significant damage to pulp fiber strength.<sup>1</sup> Carter reported the minimum  $\kappa$  number after OD is 9–10 for

\* To whom correspondence should be addressed. Tel.: (404) 894-9712. Fax: (404) 894-4778. E-mail: Lucian.lucia@ipst.gatech.edu.

**Scheme 1. Initial Set of Oxidation Reactions during Oxygen Delignification**

softwoods and 7.5–9 for hardwoods.<sup>12</sup> In the above research efforts, the final result was determined according to the change of viscosity or yield of pulp versus the decrease in  $\kappa$  number. However, the viscosity loss is related to extent of carbohydrate damage or, more specifically, the extent of oxidation of the carbohydrates; therefore, the change in the concentration of the carboxyl group, a chemical signature for the chemical oxidation process in pulp fibers, can be rationally used to express the extent of oxidation of the fiber and thus provide a relative understanding of the extent of lignin removal and its influence on pulp integrity during oxygen delignification. It is well-known that various magnesium ion compounds including  $\text{MgSO}_4$ ,  $\text{MgO}$ , and  $\text{MgCO}_3$  behave favorably for maintaining pulp viscosity during oxygen delignification.<sup>4</sup> However, these magnesium compounds also tend to decrease lignin removal from the pulp. It is known that the phenolic hydroxyl group in the residual lignin of pulp is required for a lignin reaction to occur with oxygen with subsequent lignin removal under alkali-oxygen conditions. The chemical phenol is similar to the phenolic lignin units in structure and can take part in the reaction with oxygen under alkali to produce active oxygen species, as shown in Scheme 1, which can delignify pulp. Meshitsuka<sup>15</sup> proposed that the reaction of phenolic compounds with oxygen produces active oxygen species, which can degrade nonphenolic model compounds. Chen and Lucia<sup>16</sup> proposed that phenol can protect fiber by reacting with the hydroxyl radical that is produced during the reaction of oxygen with phenolic lignin.

The present work demonstrates that a mixture of magnesium sulfate and phenol behaving as a protector system for different  $\kappa$  number pulps has a synergistic effect on the pulp selectivity of high  $\kappa$  pulps, i.e., the maintenance of pulp viscosity relative to lignin removal. Furthermore, analyses of the pulp fibers indicate that there is indeed a practical limitation for lignin removal without incurring significant selectivity loss.

## Experimental Section

**Materials.** All chemicals and reagents were commercially purchased from Aldrich, Fischer, or EM Science. Softwood kraft pulps were obtained from a kraft pulp mill with  $\kappa$  numbers of 60, 40, and 20.

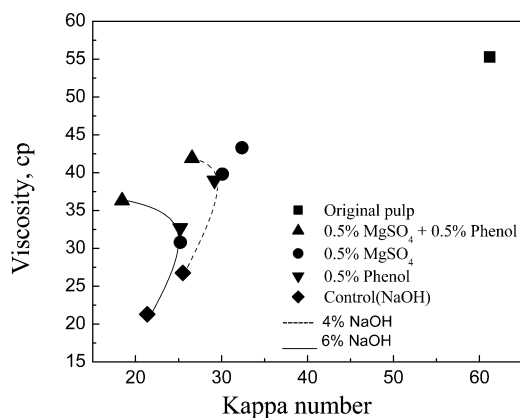
**Oxygen Delignification.** Oxygen delignification was performed in two stages without washing between stages. The first stage was carried out at 12% solids content and 2–5% alkali on pulp under a pressure of 135 psi  $\text{O}_2$  at 90 °C, whereas the subsequent stage was performed under a pressure of 80 psi of  $\text{O}_2$  at 100 °C without washing or adding more chemicals. A 1-L

pressurized reactor equipped with a stirrer and temperature controller (PARR-4551, Parr Instrument Co., Moline, IL) was used to conduct oxygen delignification of loblolly pine kraft pulps with  $\kappa$  numbers of 20, 41, and 62. Forty grams of pulp (oven dried) was mixed with the aqueous solution in the reactor to give a pulp consistency of 12%. The desired  $\text{MgSO}_4$  and  $\text{NaOH}$  charges on the pulp with the direct addition of magnesium sulfate, phenol, or a mixture of both as additives in the reaction system on an oven dried pulp percentage basis were delivered at this time. The reactor was closed and set into the heating vessel. Pressurized oxygen was then introduced into the reactor to pressurize the reactor to a desired pressure. The first stage was carried out at 12% solids content and 2–5% alkali on pulp under a pressure of 135 psi of  $\text{O}_2$  at 90 °C, whereas the subsequent stage was performed under a pressure of 80 psi  $\text{O}_2$  at 100 °C without washing or adding any additional chemicals. At the end of each experiment, the reactor was opened quickly and the filtrate squeezed out of the pulp into a sample bottle for carbonate analysis. The pulp slurry was filtered through a Büchner funnel and washed completely for  $\kappa$  number determination. All oxygen delignification experiments were done in triplicate for reproducibility and demonstrated a standard deviation in the final pulp measurements of approximately 3%.

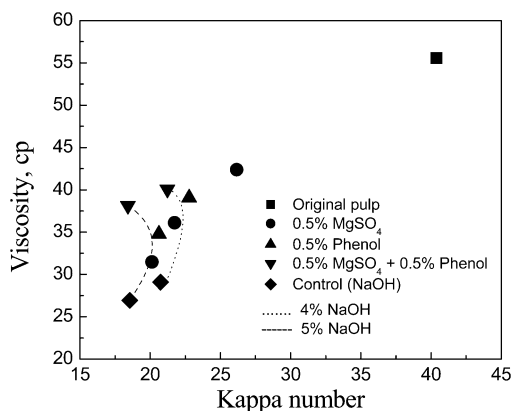
$\kappa$  number and viscosity were determined according to the following TAPPI methods:  $\kappa$  number of the pulp was determined according to TAPPI Standard Method T236 cm-85, and viscosity of the pulp was determined according to TAPPI Standard Method T230 om-94.

**Analysis of the Chemical Functional Groups in Wood Pulp Fibers.** The analysis of carboxyl groups in pulp was accomplished using phase conversion reaction headspace gas chromatography (HS-GC) based on a commercial headspace GC system (Autosampler, HP-7694; GC, HP-6890, Agilent Technologies, Palo Alto, CA) with a capillary column (model GS-Q, J&W Scientific Inc., Folsom, CA). The pulp samples were first pretreated using 0.10 mol/L hydrogen chloride acid solution for 1 h at room temperature under magnetic stirring at a constant speed. The pulp sample was then washed by ionized water several times until its pH was neutral. The dried pulp sample was accurately weighed and placed in a headspace sample vial, and bicarbonate solution was then added to react with the carboxylic acids on the pulp sample in the closed sample vial, which formed carbon dioxide that was released to the headspace. The carbon dioxide could then be measured by a thermal conductivity detector in the GC system. A near complete conversion of carboxylic acids to carbon dioxide was achieved within 10 min at 60 °C. A detailed method description has been presented in previous work.<sup>13</sup> The measurements of hexenuronic acid (HexA) content in pulps were done using established techniques.<sup>14</sup> In this method, exactly 0.050 g of pulp was hydrolyzed with a mixture of 22 mmol/L (0.6%) mercuric chloride and 0.7% sodium acetate at 60–70 °C for 30 min. After the solution was cooled to room temperature, spectroscopic measurements of the absorption of the solution at 260 and 290 nm were obtained. With the absorbance data from the UV measurement on the resulting solution, the HexA content in pulps was calculated according to a previous work.<sup>14</sup>

**Determination of Carbonate in Effluent Liquor of Oxygen Delignification.** A 1 mL of 4 N  $\text{H}_2\text{SO}_4$  was



**Figure 1.** Selectivity of oxygen delignification for the pulp having  $\kappa$  number 60.

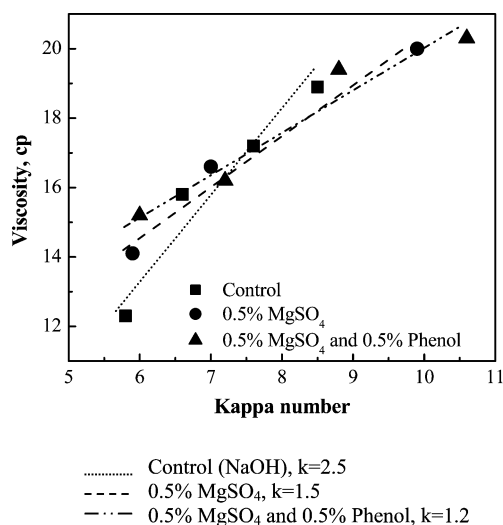


**Figure 2.** Selectivity of oxygen delignification for the pulp having  $\kappa$  number 40.

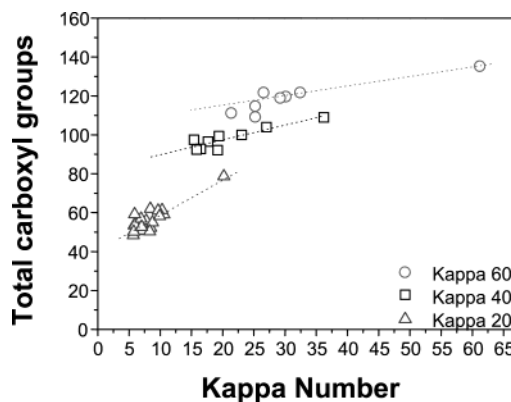
added in a 20 mL vial, and the vial was sealed. A 100- $\mu$ L amount of effluent liquor from the oxygen delignification runs was injected into the vial, in which the amount of carbon dioxide was determined using head-space gas chromatography. The amount of carbonate in liquor was expressed in moles after measurement of the carbon dioxide.

## Results and Discussion

**Influence of Magnesium Sulfate and Phenol on the Oxygen Delignification Process.** Figures 1–3 demonstrate that the viscosity changed with  $\kappa$  number under controlled oxygen delignification conditions for the pulps with  $\kappa$  numbers 60, 40, and 20. It was found that the selectivity of delignification (change in  $\kappa$  over change in viscosity) among the  $\kappa$  sets was quite different. When magnesium sulfate or phenol was added to the OD system, the viscosity of the pulp changed less than that observed for the control, which indicated that these two additives were able to protect the fiber during OD, although delignification was reduced. Furthermore, when both of these compounds were added in the system at the same time, a synergistic effect was observed for protection of the pulp fiber and improvement of lignin removal. The parabolic curves shown in the figures are the cases of OD with the same concentration of sodium hydroxide on the pulps. The higher the  $\kappa$  number pulp employed for OD, the more obvious is the synergistic effect for the selectivity of delignification. When a pulp with  $\kappa$  number 60 was subjected to oxygen delignification in the presence of both  $\text{MgSO}_4$  and phenol, the viscosity difference is 16 cP between  $\text{MgSO}_4$ /phenol and



**Figure 3.** Selectivity of oxygen delignification for the pulp having  $\kappa$  number 20: (···) control (NaOH),  $k = 2.5$ ; (---) 0.5%  $\text{MgSO}_4$ ,  $k = 1.5$ ; (- · -) 0.5%  $\text{MgSO}_4$  and 0.5% phenol,  $k = 1.2$ .

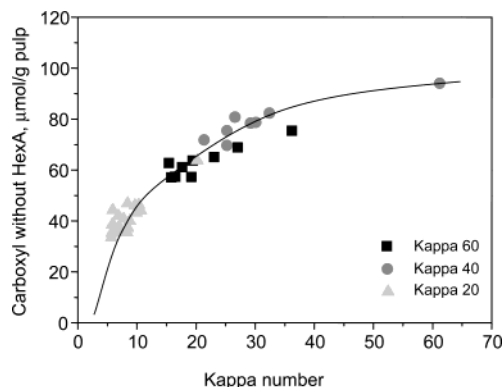


**Figure 4.** Carboxyl group on the pulp fiber for different  $\kappa$  number pulps.

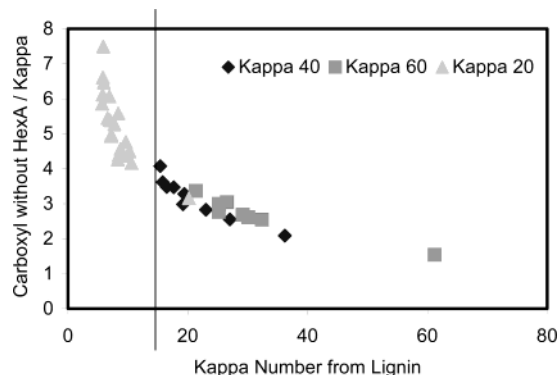
the control. When the  $\kappa$  number of the pulp is 40, the difference in viscosity is approximately 10 cP units. When the  $\kappa$  number of pulp is 20, the protection of the fiber by  $\text{MgSO}_4$  is not as obvious as observed for the high  $\kappa$  number pulp; therefore, the synergistic effect for selectivity in delignification is not as evident for the low  $\kappa$  pulps as it is for the high. Nevertheless, the slopes ( $k$ ) are different in the change of viscosity versus  $\kappa$  number as shown in Figure 3 using the different additives. With an increase in the alkali used in OD, both the  $\kappa$  number and the viscosity of pulps decreased. The value of the slope is smaller with both  $\text{MgSO}_4$  and phenol as additives than that with only  $\text{MgSO}_4$  or without additives.

**Oxidation of Pulp Fiber during Oxygen Delignification.** In general, the viscosity of pulp is used to determine the benefits of pulp bleaching on the selectivity of delignification since the viscosity is related to the degree of cellulose polymerization and molecular weight. However, the TAPPI method of determining viscosity is limited to a narrow range of viscosity and cannot be used for high  $\kappa$  number pulps. However, the carboxyl group on pulp can be used to express the oxidation of the fiber during oxygen delignification. Lignin in pulp possesses carboxyl groups, so a high  $\kappa$  number pulp may contain a high content of carboxyl groups, as shown in Figure 4. In every experimental group, the right point represents the original pulp, which indicates that the highest content of carboxyl groups in the pulp is





**Figure 5.** Carboxyl groups without HexA on the pulp fiber.



**Figure 6.** Carboxyl index without HexA for pulp fiber.

correlated with the highest  $\kappa$  number. It was found that the total carboxyl group decreased with lignin removal during oxygen delignification. However, the total concentration of carboxyl groups includes the contribution from hemicellulose. It is known that the carboxyl group may derive from two principal components in pulp: lignin and hexenuronic acids (HexA) that are derived from hemicellulose. Although HexA contributed to carboxyl group levels in pulp, HexA remains essentially the same during the oxygen delignification.<sup>17</sup> We also determined these levels in the pulps. Figure 5 illustrates the relationship of the carboxyl group in the pulp without HexA to  $\kappa$  number. It was found that the change in the carboxyl levels for all the pulps having different  $\kappa$  numbers followed a regular hyperbolic curve, despite the  $\kappa$  number of the original pulp, as opposed to the data in Figure 4.

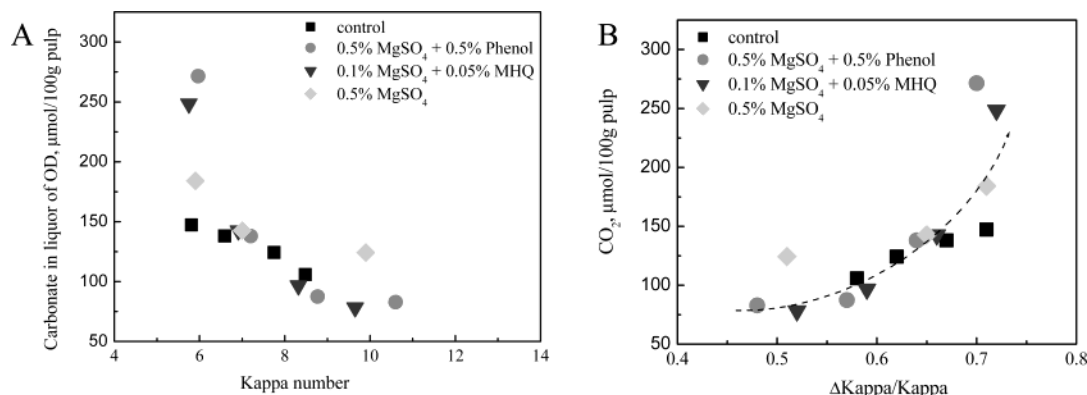
To show the degree of oxidation of pulp during the oxygen delignification process, the relationship of the ratio of carboxyl group content to  $\kappa$  number is shown in

Figure 6. It was found that the ratio changed very slowly when the  $\kappa$  number of pulp was greater than 7, but afterward the ratio increased sharply. In this case, the carboxyl groups derive almost completely from the residual lignin and cellulose in pulp. It is entirely possible that the pulp cellulose became degraded as the oxidation continued beyond a  $\kappa$  number of 7, but this point will be clarified shortly. At that point, the spike in carbon dioxide concentration paralleled the carbonate concentration in the liquor of oxygen delignification as shown in Figure 7 since  $\text{CO}_2$  is converted to carbonate in basic solution.

Alternate additives such as 3-methoxyhydroxyquinone (MHQ) were employed in the latter case to determine any differences in the mechanism of degradation leading to carbonate in the liquor. In Figure 7 it is shown that there indeed exists a limitation to oxygen delignification regardless of the additive employed. Whether or not additives are used in the reaction system, carbon dioxide is formed quickly when the  $\kappa$  number of pulp is below 7 (Figure 7A) or the degree of delignification is more than 65%, i.e.,  $\Delta\kappa/\kappa$  (change in  $\kappa/\kappa$ ) is greater than 0.65 (Figure 7B). It has already been illustrated that a lignin structure is converted to muconic acid and a subsequent methyl ester derivative during oxygen delignification.<sup>18</sup> Indeed, further oxidation of these compounds produces carbon dioxide. However, the amount of residual lignin in the pulp is limited, which is not likely to cause the levels of  $\text{CO}_2$  to increase as sharply as shown. Therefore, the majority of  $\text{CO}_2$  in the liquor must come from oxidation of the major component of pulp, i.e., cellulose, since it has been shown that the viscosity reduction at this point (level of cellulose damage as evidenced by selectivity drop) is extremely sharp which definitively correlates with changes in the cellulose component of pulp. It is thus reasonable given the latter arguments to halt oxygen delignification (at a  $\kappa$  of 7) before the production of  $\text{CO}_2$  since its levels most likely signal the onset of cellulose oxidation.

## Conclusions

The oxygen delignification industrial process is a chemically efficient and environmentally benign technology for offsetting effluent loading during pulp bleaching processes. Additives that behave as fiber protectors have become important components in this process for reducing fiber strength damage and improving the selectivity of delignification. This study examined additive-enhanced oxygen delignification of pulps with  $\kappa$  numbers 60, 40, and 20 under alkali oxygen condition



**Figure 7.** Carbonate formed in the liquor during oxygen delignification.

using  $\text{MgSO}_4$ , phenol, and  $\text{MgSO}_4$ /phenol. The results showed that there is synergistic effect with  $\text{MgSO}_4$  and phenol during oxygen delignification. This synergistic effect is more obvious for the high  $\kappa$  number pulps than that for low  $\kappa$  number pulps, perhaps owing to the greater proportion of lignin units to oxidize. The final  $\kappa$  number of pulp is a significant criterion for understanding the limits of oxygen delignification. To clarify, it was determined that the change in the carboxyl group content in pulp is a satisfactory parameter to demonstrate the degree of oxidation incurred by the pulp. Thus, the determination of carboxyl group on the pulp fiber and analysis of the carbonate in the effluent liquor demonstrated that the  $\kappa$  number of softwood kraft pulp cannot go below 7 during oxygen delignification despite using additives since cellulose degradation becomes the dominant process in oxygen delignification of pulp.

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