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Advances in Understanding the Basics of the First Alkaline Extraction Stage in Bleaching

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ADVANCES IN UNDERSTANDING THE BASICS OF THE FIRST ALKALINE EXTRACTION STAGE IN BLEACHING

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ABSTRACT

Recent proposed changes in the environmental performance of kraft bleaching operations have focused extensive research on new bleaching agents and improvements in chlorine dioxide. Less attention has been directed towards the subsequent alkaline extraction stage. Although researchers have identified the optimal charge of NaOH to promote delignification and AOX reduction during an E-stage, little is known of the complex reactions involved in this process.

This paper explores the chemistry involved in a conventional E, E+O, and E+O+P stage after the initial D stage. Employing advanced spectroscopic techniques, we have demonstrated that the concentration of carboxylic acid groups generated in an E and E+O are comparable, suggesting oxygen does not significantly enhance carboxylic acid formation. Hydrolysis of methyl ester structures formed during the preceding ClO_2 stage appears to be the main reaction causing the formation of carboxylic acid groups during the alkaline extraction. Although phenolic groups were found to be depleted during the alkaline extraction, this reaction was not found to significantly increase the carboxylic acid content. Bleaching studies have shown the chemistry of the alkaline extraction stage to influence subsequent chlorine dioxide brightening reactions employing D(E*); E*= E, E+O, E+O+P.

INTRODUCTION

Pulp bleached in an acidic ClO_2 stage contains a large portion of the lignin which can only be removed by a subsequent treatment in an alkaline environment at elevated temperatures, termed an alkaline extraction stage. Alkaline extraction stage conditions including exit pH, temperature, time, and the previous ClO_2 stage conditions have been shown to affect the amount of residual lignin (1,2).

A cursory literature review of NaOH extraction chemistry reveals its primary function is the neutralization of partially degraded acidic fragments. The resulting anionic forms increase the lignin's solubility thereby increasing delignification (3). Alkaline extraction chemistry is also beneficial in reducing AOX through base-catalyzed hydrolysis reactions. As much as 70% of organically bound chlorine in chlorinated kraft pulp can be removed during alkaline extraction (2). Elimination of chlorine from lignin occurs via a nucleophilic displacement reaction, where either OH⁻ or an neighboring hydroxyl (forming an intermediate oxirane) acts as the nucleophile (4).

Model compound studies have shown a similar nucleophilic addition of hydroxide ions to take place in non-chlorinated quinone structures of lignin model compounds. This reaction produces a hydroxy-substituted catechol or a carboxylic acid substituted cyclopentadiene (5). Several model compound studies have also briefly looked at the decomposition of ortho- and para-quinone structures in alkaline extraction conditions (6 - 8). These studies hypothesize the existence of base catalyzed condensation reactions of ortho- and para-quinone structures. The postulated reaction forms bi-phenyl linkages and converts carbonyl groups to phenolic hydroxyl groups.

Our research has suggested that an additional alkaline extraction reaction important to lignin removal exists. This study compares ClO_2 bleached residual lignins to alkaline extracted residual and dissolved lignins by NMR spectroscopy. The results indicate the introduction of carboxylic acid groups to be a major chemical modification which occurs during alkaline extraction. The carboxylic acid group formation combined with evidence that the ester linkage of a methyl ester group does not survive the alkaline extraction leads to the conclusion that the ester linkages become saponified, creating additional aliphatic carboxylic acid groups.

EXPERIMENTAL PROCEDURES

The residual lignins from the kraft pulps were isolated employing an acid hydrolysis technique that has been commonly used to isolate lignin from wood and kraft pulps (9 - 12). Effluent lignins were isolated by a similar technique, using much milder acid conditions. The procedure used starts with collecting the effluent from the first washing of the pulp and concentrating it to a solid form using evaporation under reduced pressure and then freeze drying. The solid form of the effluent was then dissolved as a 1% solution in 9:1 dioxane:water (v/v) with 0.01 M HCl (pH = 2.0). The solution was refluxed under argon for 1 hr, after which it was filtered through celite and neutralized to pH 7. The para-

dioxane was removed through evaporation under reduced pressure, dialyzed, and freeze dried. The effluent lignins were subsequently purified with a pentane extraction.

The kraft pulps were bleached with chlorine dioxide (D stage) followed by an alkaline extraction. The chlorine dioxide stages were all performed in a Quantum Technologies mixer. A kappa factor (defined as total active chlorine charge/kappa number) of 0.20 was used. The pulps, at 10% consistency and 2.5 pH, were preheated to 45°C in the mixer and an aqueous solution of ClO_2 added to the pulp. The pulps were mixed every 5 minutes for 45 minutes and then removed from the mixer. They were then thoroughly washed with DI water (15L of water for every 200 oven dry grams of pulp and filtered, resulting in a fully washed ClO_2 bleached pulp. This pulp was split and one portion extracted with NaOH and the other portion saved for residual lignin isolation. Slightly different conditions were used for the initial experiments (data in Figures 1 and 3). These ClO_2 bleaching reactions were performed at an initial pH of 4.5 and were reacted for 30 minutes.

The alkaline extraction was performed immediately after the ClO_2 bleaching reaction. The extraction was done in a continuously stirred reactor at 70°C for 60 minutes. Sodium hydroxide was added at a 2.0% charge for the reactions without oxidant reinforcement and a 2.5% charge for the reactions including oxygen. The oxygen pressure profile for the E+O and E+O+P extraction stages used an initial pressure of 60 psig, decreasing 12 psi every 5 minutes. A 0.5% H_2O_2 charge was used in the E+O+P alkaline extraction stages. An alkaline extraction of pulp performed in the absence of oxygen was accomplished through multiple freeze-thawing under argon. The oxygen free pulp was transferred to the reactor frozen, heated to reaction temperature at which time a solution of 1N NaOH was added (also frozen-thawed under argon multiple times to remove the oxygen). The reaction was performed under a steady flow of argon. At the end of the reaction the pH was lowered to 7.0 with 1.0 N HCl. This stage is denoted E+A in this paper as it was done under argon.

Isolated D stage residual lignin was treated under alkaline extraction stage conditions with and without oxygen reinforcement and with the total exclusion of oxygen. The residual lignin in a water solution (1.8 g/L) was treated with a 160% charge of NaOH (the equivalent to a normal alkaline extraction stage). In the case of the lignin treated in the absence of oxygen, the technique of multiple freezing-thawing the solution under argon was used and the reaction was performed under argon. The reaction with O_2 pressure was performed in a sealed bomb at a pressure of 60 psig, the reaction in air was performed in the same bomb without being sealed, and the reaction in argon was done inside a 3 neck

round bottom flask. The lignins were collected after these treatments by acidifying the solutions to a pH of 2.0 and washing the precipitates 3 times with DI water before freeze drying.

Structural analysis of the lignin samples was accomplished using modern NMR techniques. ^{1}H-NMR spectra of lignin were recorded under quantitative conditions using a 30° pulse and 7 second pulse delay. For each spectra 750 acquisitions were recorded and a 17 ppm sweep width was used. Underivatized lignin was first dried under vacuum for 24 hours at 40°C and accurately weighed out into a 2 ml vial. A standard solution containing pentafluorbenzaldehyde (PFB) and tetramethylsilane (TMS) in DMSO-d_6 was made and added to the lignin. The standard solution was made by adding PFB (0.1881g) and diluting to 10.0 ml with DMSO-d_6. An aliquot of this solution (0.250 ml) was then added to the lignin. An additional 0.250 ml of DMSO-d_6 was added to the sample and stirred vigorously. The solution was then transferred into a 5 mm NMR tube and the ^{1}H-NMR spectrum recorded.

^{13}C-NMR spectra were recorded under quantitative conditions following standard literature methods (13). The solvent used for all lignin samples was DMSO-d_6. NMR samples typically contained 300-400 mg lignin/ml DMSO for residual lignins and 550-650 mg lignin/ml DMSO for effluent lignins. All samples were placed in a 5 mm NMR tube (sample volume 0.45-0.50 ml) and heated to 50°C in the Bruker QNP probe.

Lignin hydroxy groups were further characterized by derivatization with of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane and subsequently analyzed by ^{31}P-NMR following literature methods (14).

Pulp properties of kappa, viscosity, and brightness were performed according to TAPPI Standards.

RESULTS AND DISCUSSION

Interesting observations were made about alkaline extraction chemistry by comparing the spectra of ClO_2 bleached residual lignins with spectra of alkaline extracted residual and effluent lignins. The quantitative ^{13}C-NMR spectra of these lignin are presented in Figure 1.
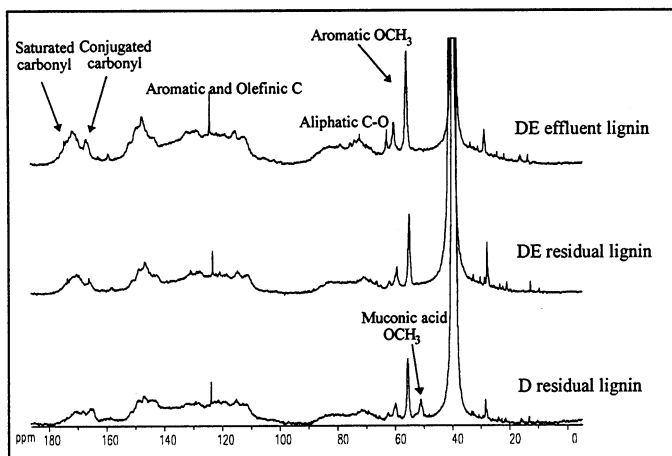
Figure 1. Quantitative ^{13}C-NMR spectra of lignin samples.

Figure 1 indicates that some important chemical modifications to the lignins have occurred during the alkaline extraction. Specifically, a comparison of the carbonyl to methoxyl signals indicates a change. In the ClO_2 bleached residual lignins, the intensity of the δ 170-165 ppm region is greater than the δ 180-170 ppm region is high. However, after the alkaline extraction the relative intensities are reversed as the δ 170 - 165 ppm (conjugated aromatic carboxylic acid) region decreases and the δ 180 -170 ppm (aliphatic carboxylic acid) region increases. The result can be partially explained by an analysis of the methyl ester methoxyl signal which is completely gone in the alkaline extracted lignins, indicating that this ester linkage did not survive the alkaline extraction. The ester linkage appears to have been saponified, creating a carboxylic acid group (shown in Figure 2). The saponification would create a carboxylic acid that would influence the chemical shift of the carbonyl group. This may partially explain the observed intensity differences in the carbonyl region.

These results led to an investigation to determine if the saponification reaction was responsible for the increase in carboxylic acid groups or if the increase was due to an autoxidation reaction with atmospheric oxygen present in a conventional E stage. To test this isolated residual D stage lignin was frozen/thawed under argon several times to remove all oxygen from the lignin containing solution. This lignin solution was then reacted with NaOH at normal alkaline extraction conditions, except for a continuos flow of argon to prevent any oxygen into the system. A second sample of the D stage lignin was reacted under typical E conditions. Both samples were then acid precipitated and washed to remove salts. ^{1}H - NMR analysis was performed on these samples as well as the starting D residual lignin. The results from the analysis (shown in Figure 3) show changes in the carboxylic acid and phenolic content from the alkaline extraction.
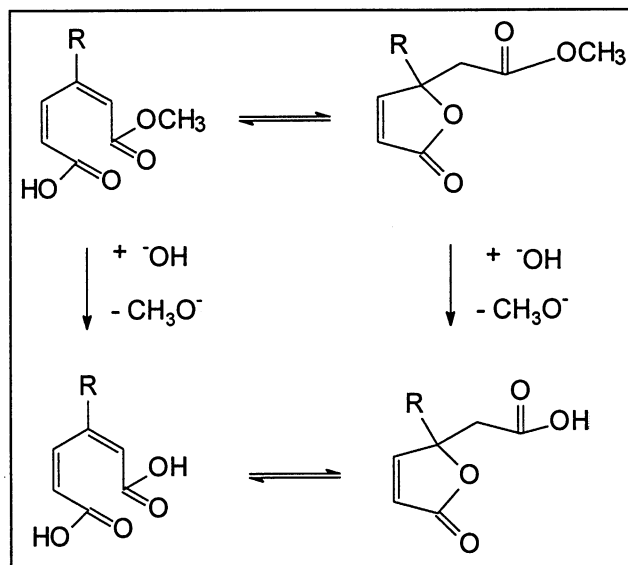

Figure 2. Saponification of the methyl ester group in muconic acid methyl ester and its cyclized lactone under alkaline extraction conditions.
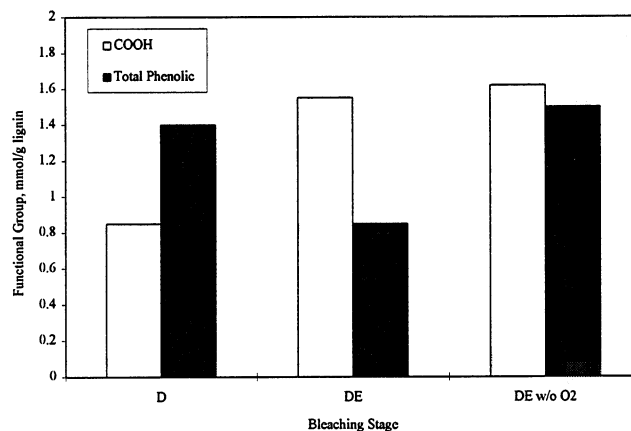

Figure 3. Carboxylic acid and Phenolic Content of Alkaline Extraction Reacted Lignins.

The results from Figure 3 indicate the carboxylic acid content to increase from the D residual to approximately the same amount regardless if oxygen was present in the system. This strengthens the hypothesis that NaOH saponification reactions are the cause of the increase in carboxylic acid content. The other result from this study is that phenolic content of the lignin only decreases if there is oxygen present in the system. This is not surprising as oxygen is theorized to react primarily with phenolic groups. However, the oxygen reaction with phenolic groups is believed to yield carboxylic acid groups. This study does not support this theorized mechanism, although it is unknown what the oxygen reaction products are.

Since this study was done using isolated lignin, a second alkaline extraction study was performed using D stage pulp

instead of isolated lignin. The D stage conditions were also slightly varied to provide more delignification. Four different alkaline extraction conditions were employed to further investigate the effect of oxidant reinforcement. The stages included a alkaline extraction with all oxygen removed from the system (designated E+A as it was done under argon), a conventional E stage, an E+O stage, and an E+O+P stage (the O and P stand for oxygen and hydrogen peroxide reinforcement, respectively). Kappa and viscosity numbers for the various bleaching stage are shown in Figure 4.
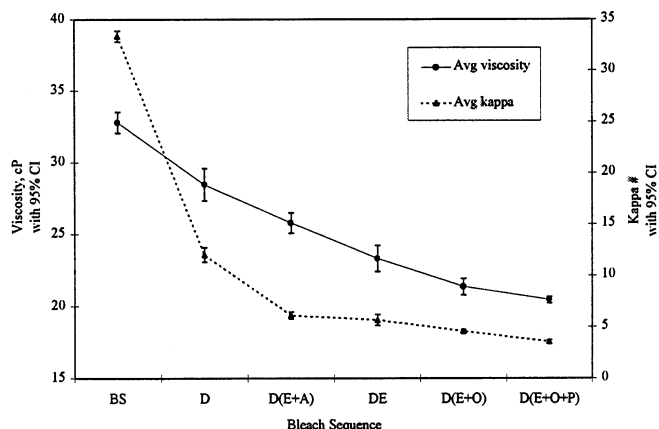

Figure 4. Bleached Pulp Viscosity and Kappa Measurements.

The residual and effluent lignin from the pulps were isolated and analyzed with ^{31}P NMR spectroscopy. An example of a typical ^{31}P-NMR lignin spectrum is shown in Figure 5.
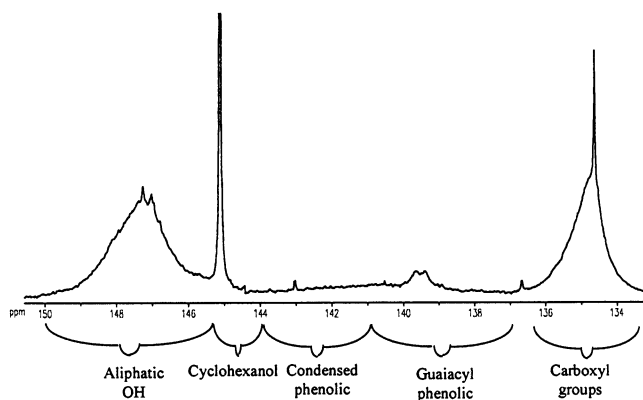

Figure 5. Quantitative ^{31}P-NMR spectra of lignin samples.

The integration regions for the various alkaline extraction conditions were tabulated for carboxylic acid functional groups of both the residual and effluent lignins and plotted in Figure 6. The results suggest that the (E) and (E+A) treatments gave the same amount of acid groups. A slight

increase in the carboxyl groups was seen with the E+O (20% increase over E) and E+O+P (17% increase over E) in the effluent lignins suggesting some additional carboxylic acid formation.
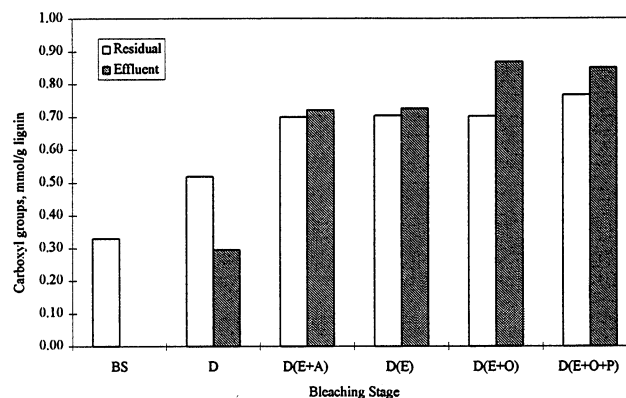

Figure 6. Carboxyl groups of various bleached lignins.

The total phenolic groups were also tabulated from the ^{31}P integration regions and were plotted on Figure 7. These results do not agree with the observations from the earlier study which saw a dramatic decrease in phenolic group content with the inclusion of even atmospheric oxygen. It is hypothesized that the lower pH used in the D stage of this study depleted the majority of reactive phenolic sites. A comparison of the D stage residual lignin between the two studies (Figures 3 and 7) supports this. The earlier study (using an initial pH in the D stage of 4.5) had a residual phenolic content of 1.5 mmol/g, which is considerably higher than the later study's (using an initial pH in the D stage of 2.5) phenolic content of 0.6 mmol/g.
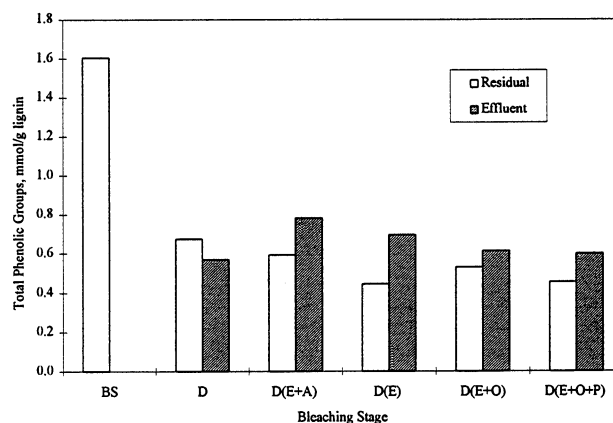

Figure 7. Total phenolic groups of various bleached lignins.

The various alkaline extracted pulps were brightened in a second D stage. The conditions used were 0.75% charge of ClO_2, 0.20% charge of NaOH (for pH adjustment) on a 10% consistency pulp at 70°C for 3 hours. The results shown in

Figure 8 indicates that the added oxidants have a profound effect on increasing brightness, even though their kappa numbers are relatively close. This suggests the oxidants of oxygen and peroxide are more beneficial in destroying lignin chromophores than in assisting delignification. Further studies are planned to explore this.
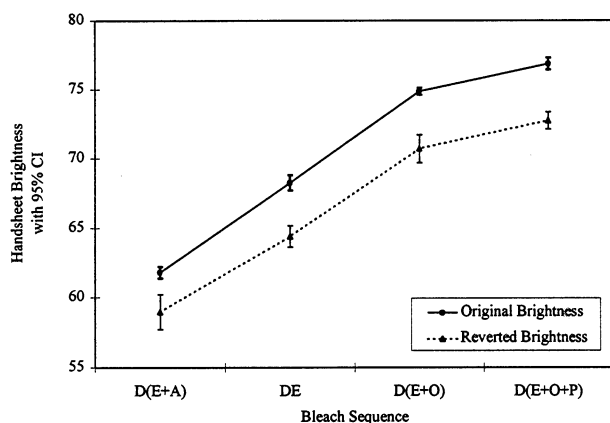

Figure 8. ISO Brightness Measurements on Handsheets.

CONCLUSIONS

During an alkaline treatment of D stage lignin, an increase in acid content was found not to be substantially affected by the presence of oxygen, indicating that the introduction of these acids is not a result of oxidation of phenolic groups by oxygen but rather from the saponification of the methyl ester group in muconic acid methyl ester by hydroxide ions. In addition to acid neutralization and base catalyzed elimination of chlorine, saponification of methyl esters appears to be a major reaction in assisting delignification. Manipulation of this reaction through pH, temperature, or time may assist in more efficiently removing oxidized lignin from the D stage.

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