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of Effluent Lignin of Various Oxidative Alkaline Extraction Stages

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Comparison of Effluent Molecular Weight Distributions of Effluent Lignin of Various Oxidative Alkaline Extraction Stages.

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ABSTRACT

The use of oxygen or hydrogen peroxide as an oxidative reinforcement in the first alkaline extraction stage has proven to be a popular method of reducing the amount of chlorine or chlorine dioxide needed in the initial delignification stage. Although the use of such a stage has become more common in pulp mills, little fundamental research has been done to study the effect of these oxidants. To study the effect of oxygen and/or hydrogen peroxide as oxidants in an alkaline extraction, molecular weight distributions were determined for various bleach sequences. The results indicate that oxygen and hydrogen peroxide are capable of reducing effluent molecular weight averages due to lignin degradation by the oxidants. The study also suggests that the oxidants are not selective for residual lignin but can be consumed by lignin already in suspension from the alkaline extraction.

INTRODUCTION

Recently proposed environmental regulations will limit the amounts of chlorine dioxide that can be employed for bleaching kraft pulps. As such, one of the easiest means of enhancing the delignification of kraft pulps will be to reinforce the first alkaline extraction stage with an oxidant. Indeed, a variety of researchers have documented the improved delignification performance of an (E+O), (E+P), or an (E+O+P) stage versus an E-stage after the D delignification stage (1, 2, 3, 4, 5, 6, 7). Despite these advances, the bleaching chemistry of advanced alkaline reinforced extraction stages remains poorly defined, and future developments in this field would be facilitated if the fundamental chemistry of this stage was understood.

Research into pulping and bleaching chemistry often involves measuring the amount of degradation of lignin through changes in residual lignin content, functional groups, and optical properties. Another less commonly used method is to study the degradation of the lignin polymer chain directly by measuring its molecular weight profile.

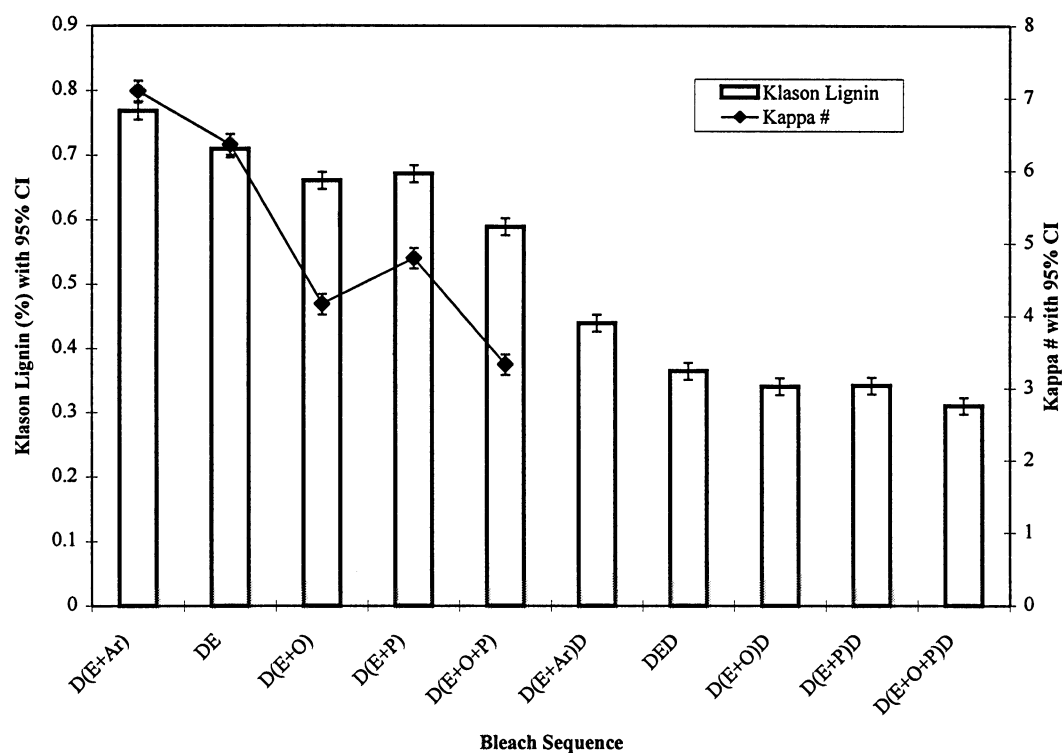
Gel permeation chromatography (GPC) is a frequently employed method of determining molecular weight profiles of lignocellulosic materials. This procedure, based on size exclusion chromatography principles, has been used to determine the molecular weight profile of various lignin model compounds (8, 9), isolated lignin (10, 11, 12), and bleaching effluent lignin (13, 14, 15). Recently, Schwantes and McDonough (16) employed a TOC detector to monitor the eluents from a GPC column and demonstrated this procedure was useful for determining the molecular weight distributions of bleach effluent lignin.

This study will compare the use of various amounts and types of oxidant reinforcement in an alkaline extraction stage after a ClO_2 delignification stage. The study employs GPC to measure the molecular weight profiles for bleaching effluents along with more conventional pulp characterization tests, including kappa #, Klason lignin %, viscosity, and ISO brightness. The results of this study provide insight into the effect these oxidants have on the lignin entering the alkaline extraction stage.

RESULTS AND DISCUSSION

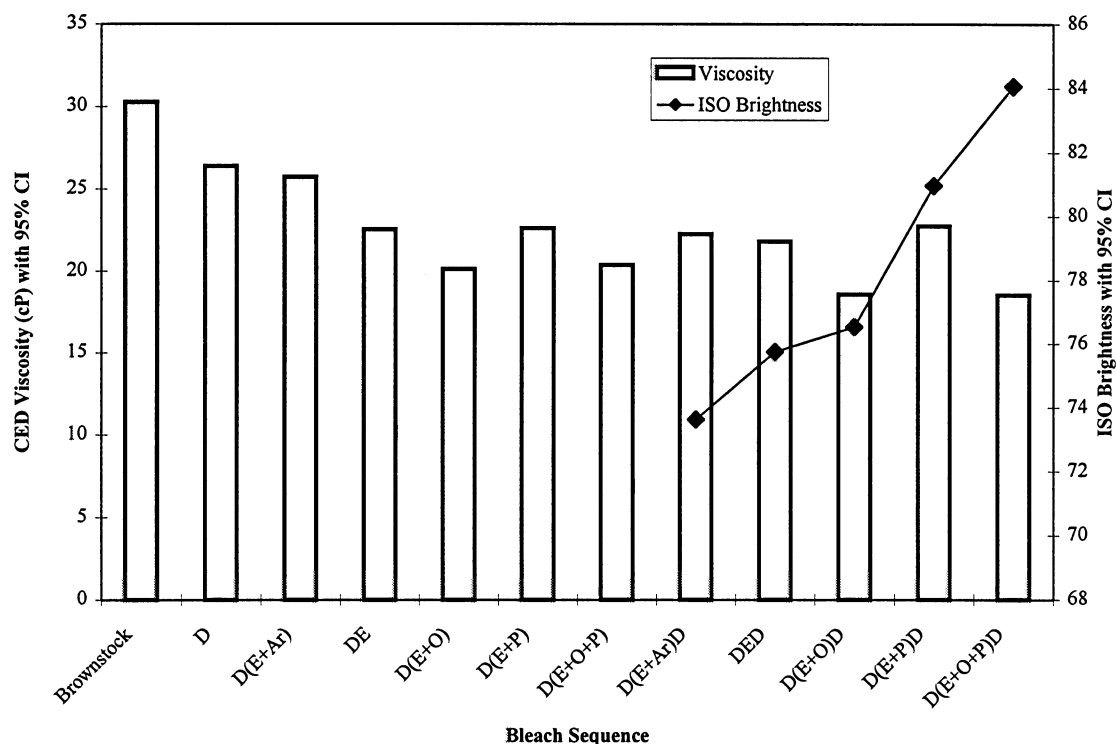
Pulp Characterization

As a preliminary investigation into the bleaching chemistry of an alkaline extraction stage, a softwood kraft pulp was bleached with a 0.20 kappa factor D stage. The resulting pulps were then alkaline extracted under a variety of conditions, including E, (E+O), (E+P), and (E+O+P) conditions. In addition to these treatments, the E-stage was repeated in the absence of oxygen by purging the pulp and the reactor with argon. The argon purged E stage, referred to as (E+Ar), was examined so as to determine how much delignification occurs in an E stage due to dissolved oxygen from the air. The changes in lignin content for the alkaline extracted pulps before and after a D1 stage are summarized in **Fig. 1**. A comparison of lignin content of the (E+Ar) and E pulps indicates that ambient dissolved oxygen aids lignin removal by 2.4%. Furthermore, as to be expected from literature results, the (E+O+P) stage was most effective at removing lignin from the D delignified pulp. These differences in lignin content after the initial alkaline extraction stage were narrowed by the D1 stage, but the overall trend remained the same.



1. Lignin contents of a 30.0 kappa softwood kraft pulp bleached with 0.20 kappa factor of ClO_2 and treated to various alkaline extraction conditions and a 0.75% D1 charge. Klason content of D delignified pulp was 2.5%, and kappa number was 14.

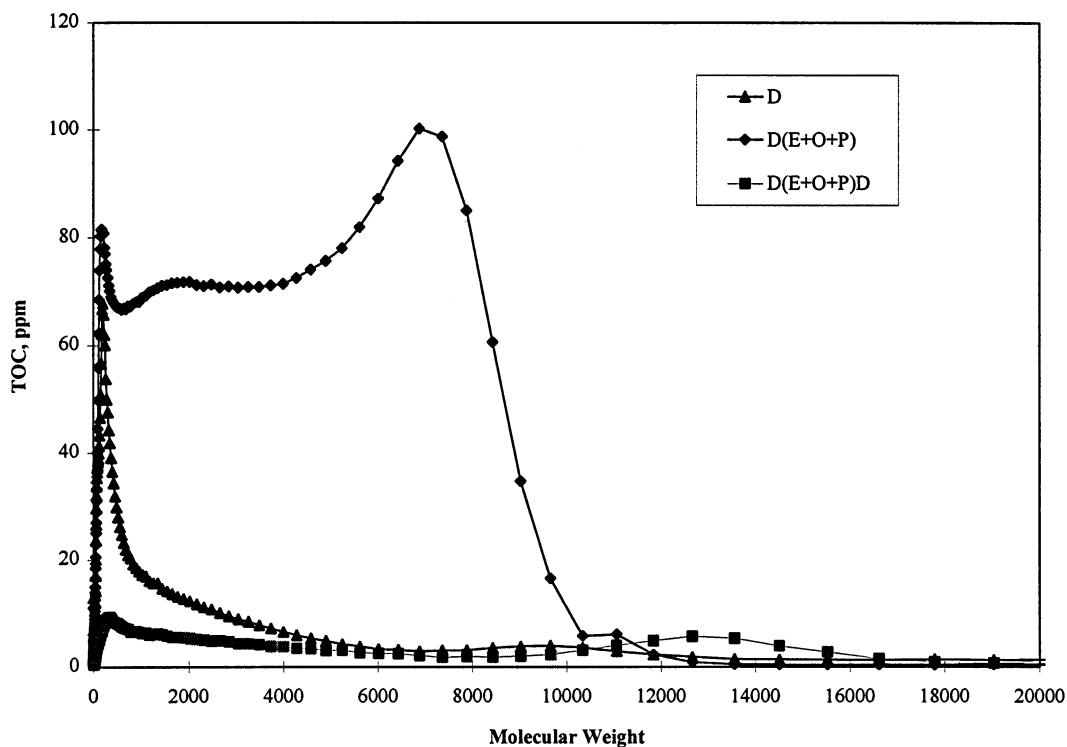
Cupriethylenediamine viscosities are also shown with their 95% confidence intervals in Fig. 2. Although viscosities of all the samples are high enough to not reduce the final sheet strength, cellulose degradation was observed with added oxidation. It is interesting to note that the oxygen reinforcement in the alkaline extraction causes more cellulose degradation than hydrogen peroxide. Hydrogen peroxide also shows advantages in brightness values as there is a substantial increase in brightness with alkaline extraction stages containing hydrogen peroxide oxidant reinforcement.



2. Pulp viscosity and ISO brightness.

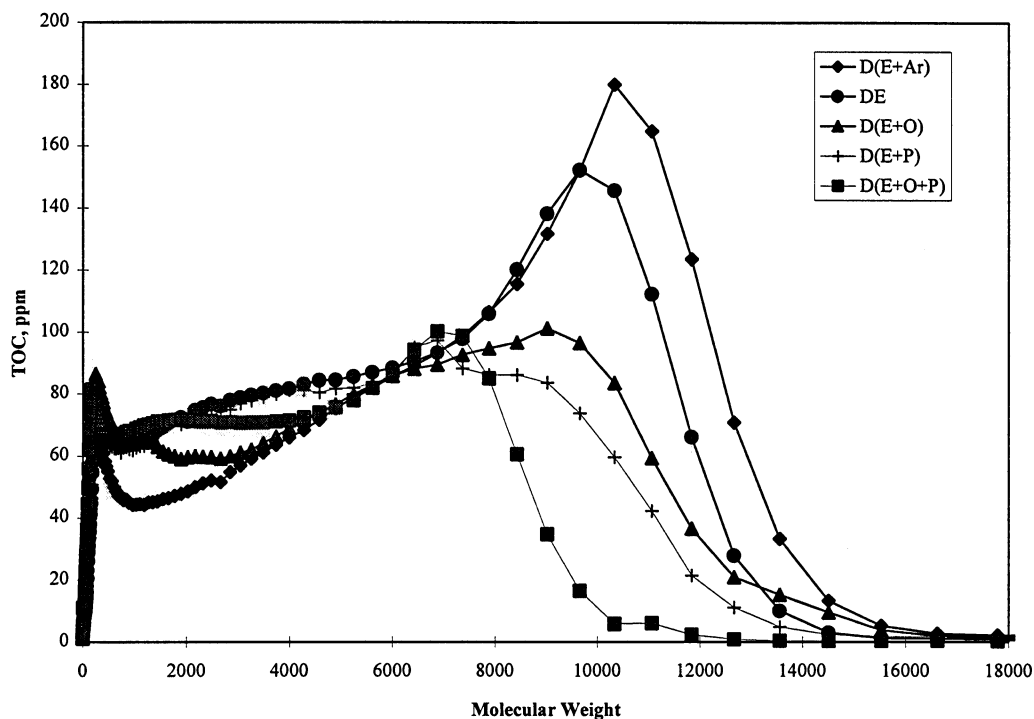
Molecular Weight Distributions of Bleach Effluents

The fundamental processes contributing to the observed differences in bleaching efficiency were further explored by studying the molecular weight distributions of the DE* and DE*D bleach effluents. Effluent samples from the various bleach stages were characterized using the Schwantes GPC-TOC method for analyzing bleach effluents (16). Typical molecular weight distributions for the first three bleaching stages are shown in **Fig. 3**. The figure depicts the D delignification stage to peak at a MW of approximately 300 and quickly tail off. This is expected as the initial D stage effluent is acidic (pH ~ 2), allowing only small molecular weight fragments to be soluble. The D(E+O+P) effluent shows a bimodal distribution with a higher molecular weight distribution, which also is expected because this effluent is alkaline (pH ~ 11). The D(E+O+P)D stage also shows a bimodal distribution but considerably less organic matter (as measured by TOC). The depletion of low molecular weight fragments and presence of high molecular weight fragments could be attributed to highly condensed structures being oxidized in this stage and becoming soluble through addition of hydrophilic functional groups instead of polymer chain degradation. These results agree relatively well with earlier work done on D and D(E+O) effluent lignin (15).

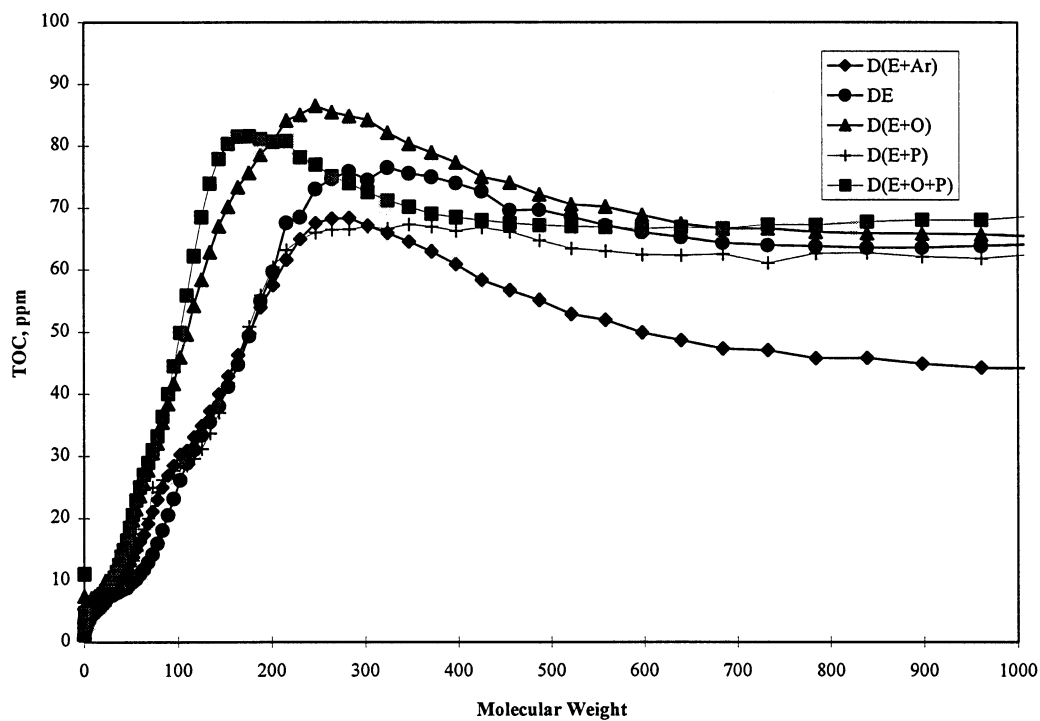


3. Typical molecular weight distributions.

The molecular weight distributions of the five alkaline extractions with different oxidant reinforcements were measured and are shown in **Fig. 4**. The figure clearly shows the alkaline extraction effluent's molecular weight decreases with added oxidant, suggesting that the lignin fragments released into the effluent are being oxidatively degraded. The low molecular weight fragments (< 1000) were plotted separately in **Fig. 5**. This figure displays an enrichment in low molecular weight fragments with increase oxidant reinforcement, as is expected from the cleavage of high molecular fragments.



4. Molecular weight distributions of alkaline extractions with different oxidant reinforcement.

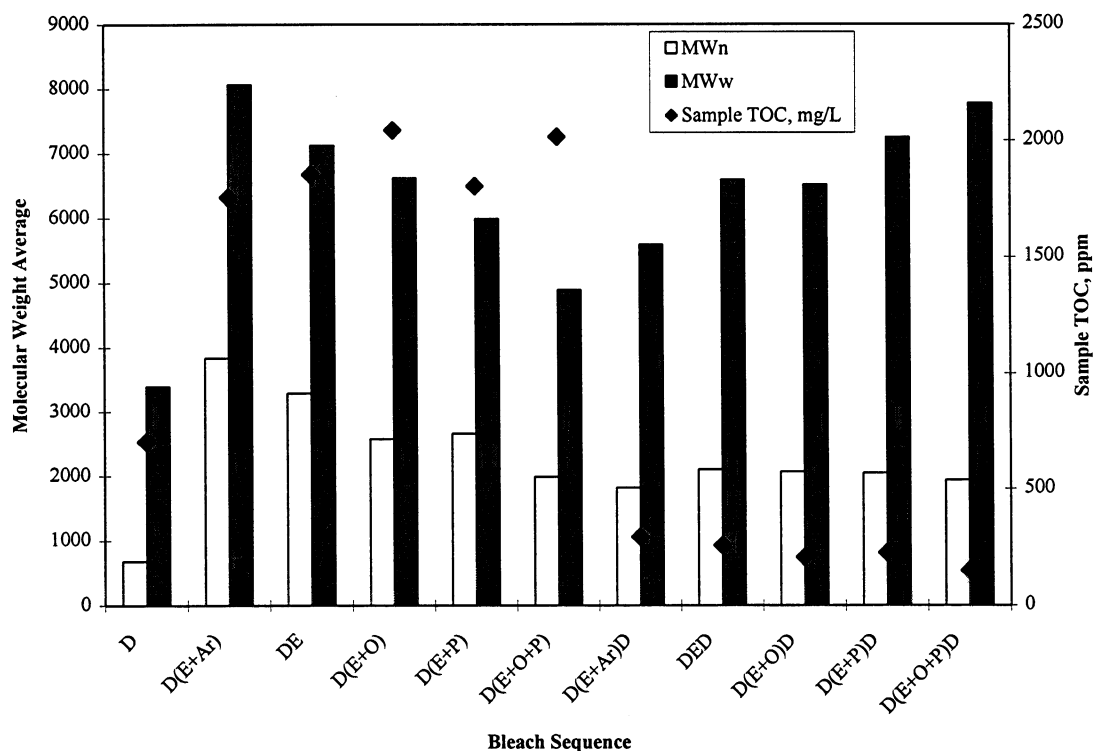


5. Molecular weight distributions of the low molecular weight distribution for effluents of alkaline extractions with different oxidant reinforcement.

The molecular weight data in **Figs. 4 and 5** were used to calculate molecular weight averages (number and weighted averages) using equations 1 and 2. These data and the results from the D1 stage molecular weight averages are shown in **Fig. 6** along with the sample's TOC to give an indication of the amount of lignin being removed in the stage. Comparison of the TOC data is possible because all stages were performed at 10% consistency.

The data in **Fig. 6** further demonstrate that the lignin degradation is due to oxidative reinforcement during the alkaline extraction. This is clearly seen in the weighted averages which measure changes in the higher molecular weight more heavily. The data also indicates relatively high molecular weight material being removed in the D1 stage. This was somewhat surprising as this is an acidic stage, perhaps suggesting highly condensed structures are being oxidized to a great enough extent that they are acid-soluble. The significance of the high D1 effluent molecular weight averages is decreased by relatively low amounts of material in the effluent.

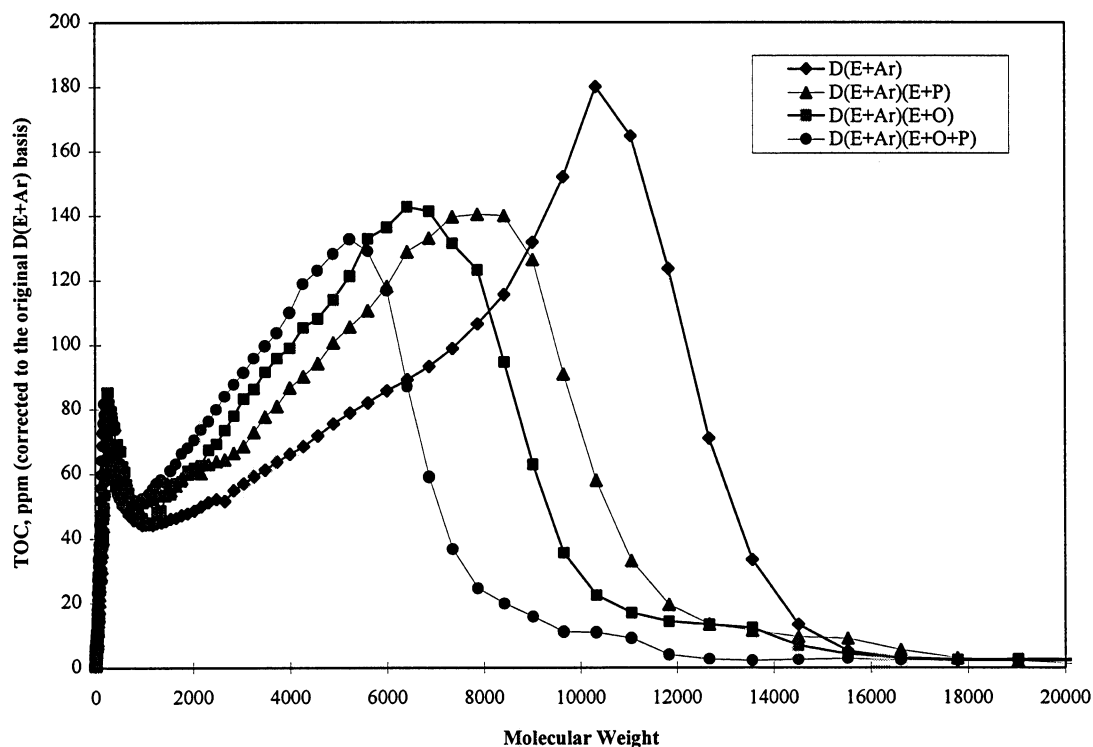
The D1 effluents also show a surprising trend of increased average molecular weight with increasing oxidant reinforcement in the previous stage. This is opposite the trend seen in the alkaline extraction effluent. Examination of the D1 molecular weight profiles provides some insight as they display the greatest changes between the D1 bleaching stages to be in the area of low molecular weight material. Depletion of low molecular weight material in the previous alkaline extraction stage appears to influence the molecular weight average in the subsequent D1 stage.



6. Molecular weight averages for different bleach stages.

Oxidation of Effluent Lignin Without Pulp Studies

As anticipated oxidant reinforcement is able to degrade lignin, decreasing its molecular weight average. However, the molecular weight profile data suggest that the lignin in the effluent is being oxidized as well as the residual lignin. This would represent a waste of the oxidant as this lignin has already been removed from the fiber. To further test if effluent lignin can be substantially oxidized, effluent from the alkaline extraction done without any oxygen (E+Ar) was subjected to peroxide and oxygen at concentrations similar to those used in stages done on pulp. Additional NaOH was added to equal the extra 0.5% used in the (E+O), (E+P), and (E+O+P) stages. The results of these reactions are shown in molecular weight profiles in Fig. 7. TOC data for the oxidized effluent were normalized to the original (E+Ar) level to correct for dilution effects. The data clearly show that the oxidant is able to decrease the molecular weight of effluent lignin, strengthening the hypothesis that some of the oxidant reinforcement in an alkaline extraction is wasted on effluent lignin.



7. Oxidation of effluent lignin by oxygen and hydrogen peroxide.

CONCLUSIONS

The data in this paper suggest that oxidant reinforcement of oxygen and hydrogen peroxide in an alkaline extraction after a ClO_2 delignification stage is able to degrade lignin and decrease its molecular weight. Although oxidant reinforcement with hydrogen peroxide and oxygen was shown to be beneficial in increasing delignification and

brightening the pulp, its usage may not be optimized. This is hypothesized as the degradation of the lignin by these oxidizers does not appear to be limited to residual lignin remaining in the fiber, but also occurs to lignin already in solution from NaOH reactions. As more lignin is present in the effluent then remains residually in the fiber during an alkaline extraction, a substantial amount of the hydrogen peroxide and oxygen may be wasted oxidizing lignin that is already free of the fiber.

EXPERIMENTAL

Pulps

Kraft pulp was obtained from single Loblolly pine (*Pinus Taeda*) approximately 30 years in age and free from disease. The wood was debarked, chipped, screened, and conventionally cooked in a MK digester. The brownstock was screened, washed, and then submitted to a typical D delignification stage (0.20 kappa factor) in a Quantum reactor at 10% consistency for 45 minutes at 45°C. The bleached pulp was then filtered, washed with water, and characterized for kappa #, Klason lignin %, and pulp viscosity.

Alkaline Extraction

The D delignified pulp was added to a continuous stirred pressure reactor, and the consistency was adjusted to 10%. The pulp was then warmed to 70°C; bleaching chemicals were added; and the mixture was stirred for 75 minutes. **Table I** summarizes the precise chemicals and charges employed during the alkaline extraction stage. Upon completion of the extraction, the pulp was removed from the reactor, filtered, and thoroughly washed. The alkaline extracted pulps were characterized in terms of kappa #, Klason lignin %, and pulp viscosity.

Bleaching Abbreviation	Bleaching Conditions Employed ^a
E	2.0% charge of NaOH, performed under atmospheric pressure.
E+O	2.5% charge of NaOH, 60 psig initially, decreasing 12 psig/5 minutes, final 50 minutes were performed at atmospheric pressure.
E+P	2.5% NaOH and 0.5% charge of hydrogen peroxide.
E+O+P	2.5% charge of NaOH, 0.5% charge of hydrogen peroxide, 60 psig initially, decreasing 12 psig/5 minutes, final 50 minutes were performed at atmospheric pressure.
E+Ar	All oxygen was removed from the pulp, and chemicals employ a freeze-thaw cycle. 2.0% charge of NaOH was used, and the reactor was slightly pressured with argon (10 psig) to prevent the introduction of O ₂ into the reactor.

^aNote: The charge of NaOH employed was selected so as to ensure that the terminal pH was > 10.5

I. Alkaline Extraction Conditions

D1 Bleaching

The alkaline extracted pulps were then bleached using a 0.75% charge of ClO_2 at 10% consistency in plastic bags immersed in a water bath 70°C for 3 hours. The pulp was thoroughly kneaded every 1/2 hour, and upon completion the bleached pulp was filtered and washed. The pulp was characterized for Klason lignin, pulp viscosities, and ISO brightness on TAPPI Standard prepared handsheets.

Pulp Characterization

The lignin content was measured using a 1/4 kappa test and a modified Klason lignin test method (17, 18). The Klason lignin method was modified to use an autoclave to speed up the sulfuric acid hydrolyzation of the carbohydrates in the pulp. The remaining lignin was filtered, dried, and weighed to give an acid-insoluble weight percentage (19). Three Klason lignin and kappa number determinations were performed for each bleach sequence except for the D1 stage, which had too low of a lignin content to perform kappa numbers. Carbohydrate degradation was measured indirectly by solvating the pulp in cupriethylenediamine and measuring these solutions' viscosity with a capillary viscometer (20). Handsheets were made from the D1 pulp at a basis weight of 150 g/m^2 using a standard test procedure (21), and then used to measure ISO brightness.

Oxidative Treatment of Effluent from (E+Ar) Stage

Effluent from the D(E+Ar) bleaching stage was reacted with oxygen and hydrogen peroxide using a 1 L continuously stirred pressurized reactor. The same oxygen pressure profile and hydrogen peroxide charge were used, calculated on a pulp weight basis. An additional 0.5% charge on a pulp weight basis was added as the oxidant reinforced alkaline extractions had this additional NaOH. These reactions were performed similarly to the alkaline extraction stage conditions (70°C for 75 minutes).

GPC Analysis of Bleach Effluents

Effluent molecular weights were measured by an aqueous gel permeation chromatography method developed by Schwantes and McDonough (16). The method passes the effluent through two Sephadex columns using a 0.1 M LiCl eluent. The discharge of the columns is into a total organic carbon (TOC) detector, which measures on a frequency of 1 sample/2.3 minutes. Low flow rates (0.65 ml/minute) allow for increased resolution due to the slow periodicity of the TOC detector. The column was calibrated using polyethylene glycol standards and methanol (giving a calibration range for molecular weights of 32 to 19,700). Tabulation of the amount of the original sample's TOC recovered within the calibration range gives an indication of holdup in the column. Number average molecular weight (MW_n) and weighted average molecular weight (MW_w) were calculated using equations 1 and 2.

$$\text{MW}_w = \sum w_i M_i \quad (1)$$

$$\text{MW}_n = \sum x_i M_i \quad (2)$$

where: w_i is the weight fraction of fraction i

x_i is the mole fraction of fraction i

M_i is the molar mass of fraction i

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