

Fundamental molecular characterization and comparison of the O, D₀, and E stage effluents from hardwood pulp bleaching

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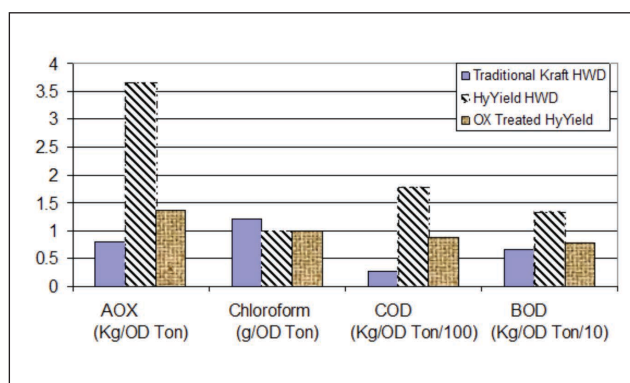
ABSTRACT: The present study characterized effluents from the O, D₀, and E stages using nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) techniques to better understand the chemical nature of the dissolved organics formed from the bleaching of a high-yield hardwood kraft pulp. Understanding the structures and molecular weight distribution of these organics is the first step in developing methods to mitigate these contaminants in the discharged effluents. The results indicated that the molecular weight distribution (MWD) of the dissolved organics from oxygen delignification effluent is broader than those from D₀ and E stage effluents. In addition, the O stage filtrate contained considerable amounts of lignin and xylan fragments, which showed its efficiency in removing such materials. The effluent from the D₀ stage contained a lower amount of high molecular weight fragments and a higher amount of low molecular weight fragments versus the O-stage filtrate. Aromatic structures were nearly absent in the D₀ stage filtrate, but the degraded organic material, presumably from oxidized lignin, contained olefinic (C=C) and carbonyl (C=O) functional groups. Furthermore, higher molecular weight fragments were detected in the E-stage effluent, presumably due to the extensive solubilization and removal of the oxidized lignin generated from the D₀ pulp.

Application: The current work is a first attempt at quantifying the organic constituents in elemental chlorine free (ECF) bleaching effluents for various bleaching sequences. These results should help direct future research efforts towards enhanced treatment and impact reduction of ECF bleaching effluents.

Sustainability and increased pulp yields are major concerns for the pulp and paper industry. As such, significant research efforts have focused on methods to enhance pulp yields from wood chips. Several potential methods have been suggested that involve increasing the kappa number of the brownstock pulp to bleaching and utilizing more selective, yield-enhancing delignification methods during pulp manufacturing [1-6]. Other efforts have focused on increasing the kappa number of the brownstock entering the oxygen delignification stage in the bleach plant [4-6]. A major drawback to employing these types of yield-enhancing processes is the increase in effluent loading associated with the bleaching process when the pulp's kappa number substantially increases [7]. One method of increasing the yield of fully-bleached pulps (from mixed southern hardwoods and eucalyptus) from about 46% to 54% (on o.d. wood) involves increasing the brownstock kappa number of the pulp from 18 to 55.

Fig. 1 shows the increases in chloroform, biochemical oxygen demand (BOD), and chemical oxygen demand (COD) in the bleach effluent loading when bleaching a 55-kappa hardwood brownstock and bleaching a 38-kappa oxygen-delignified pulp [3].

In general, a desirable sustainability effort should not only



1. Environmental emissions of high-yield hardwood pulp bleaching compared to traditional kraft pulp when bleached with D₀(EP)D₁D₂ and OX D₀(EP)D₁D₂ sequences to 88% GE brightness (with nominal 30% delignification in the O stage). Data from Hart study [3].

focus on one aspect of sustainability (e.g., pulp yield), but rather on multiple efforts from pulping to papermaking. Typically, process changes that increase the environmental footprint of the mill are not deemed to be viable even when such changes are within existing process limits. In short, the pulp and paper industry is not willing to advance on one area of the mill at the

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expense of another area of the mill that causes an environmental impact. This is a valid concern for the total well-being and sustainability of the pulp mill over the long term.

Ideally, yield enhancing process changes that increase the BOD and COD content of bleach plant effluents [1-3] would require in-process or localized treatment methods that reduce their environmental impacts before being sent to waste treatment. Specifically, treatment of the D_0 and (EP) stage bleach filtrates prior to biological waste treatment and discharge to receiving streams is of great importance.

Initial efforts have looked at the potential closure of selected wastewater streams. It was determined that the paper machine and the bleaching process produce most of the effluent. Unfortunately, total closure of the various water circuits in the bleach plant is limited due to the accumulation of contaminants in the process. These contaminants give rise to increased equipment corrosion, scale deposits, and odor emissions, as well as adversely affecting the runnability of the paper machine [8] and final sheet quality [9]. Some mills use a portion of the white water from the paper machine at the bleach plant washers. This practice has the potential to increase the BOD, COD, and calcium content of the bleach plant effluent.

According to Savant et al. [10], the most modern mills that employ best practices use about 60 m³ of water to produce one ton of paper. Bleach plant effluent can account for as much as 30% of this volume. A modern elemental chlorine free (ECF) bleaching plant with a countercurrent washing scheme generates 15 to 20 m³/a.d. ton of bleaching effluent [11]. Most mills utilize a jump-stage countercurrent washing scheme to reduce their effluent loading. This washing scheme uses D_2 filtrate as some or all of the wash water at the D_1 stage shower, and the filtrate of D_1 stage is used as shower water at the D_0 washer. Also, the filtrate of E_2 stage is used as wash water on the E_1 stage washer. A portion of the D_0 and E_1 stage washer filtrates effluents are sewerred to wastewater treatment.

Even with jump-stage countercurrent washing, the sewerred bleach plant effluent represents a major fraction of the total effluent flow going to wastewater treatment. This effluent is of concern, as it contains small amounts of organics that are recalcitrant towards wastewater biological treatment [12]. Some of these recalcitrant compounds may present ecological risks if released into the environment [13].

During the bleaching process, chlorine dioxide reacts with kraft lignin, hexenuronic acids, and other wood constituents that generate COD, BOD, and various chlorinated organic compounds [13,14]. More than 250 different compounds have been identified in bleach plant effluent, with many compounds remaining unidentified. Some of the identified compounds include chloroform, chlorate, resin acids, and polychlorinated hydrocarbons, phenols, catechols, guaiacols, furans, dioxins, syringols, vanillins, etc. [15]. These components are mainly derived from degraded lignin, carbohydrates, and wood extractives. Some polychlorinated lignin

fragments are bio-recalcitrant, toxic, and dark in color [16], which causes concern because they remain in the wastewater after biological treatment. It is suspected that the low molecular weight fraction of adsorbable organic halides (AOX), which is derived from highly chlorinated lignin, is toxic [17-20]. Such materials in bleaching effluents have been minimized by eliminating the use of elemental chlorine and hypochlorite, by increasing the use of oxygen and chlorine dioxide, and by lowering the kappa number of the pulp entering the bleach plant.

Efforts have been made to determine if specific treatments can be performed on the effluent to minimize its potential environmental impacts. Physicochemical treatment methods for wastewater treatment, such as sedimentation and flotation, coagulation and precipitation, filtration, reverse osmosis, adsorption, wet oxidation, ozonation, and advanced oxidation processes (AOPs) [21], have been reported over the past two decades for their ability to remove suspended and dissolved solids, as well as toxic compounds. Biological treatment methods, which use microorganisms, have been compared to physicochemical methods; these biological methods are considered to have a high cost-benefit, are environmentally-compatible, and are suitable for the reduction of BOD and COD [22]. Activated sludge, anaerobic lagoons, stabilization ponds, or other biological wastewater treatment processes, depending on the local conditions, have been commonly used for the wastewater treatment of pulp and paper mill effluents [23]. Anaerobic wastewater treatment has also been used.

Typical parameters for characterizing the quality of wastewater treatment include COD, BOD, AOX, total organic carbon (TOC), total suspended solids (TSS), and turbidity, as well as selected elemental levels (e.g., nitrogen, phosphorus, and sulfur) and toxicity tests. Several of these measurements have been reported for bleaching effluents from typical modern-day bleach sequences [3,13,24,25].

Current waste effluent treatment methods ameliorate a broad spectrum of organic compounds. Their performance is generally characterized using "sum parameters" such as AOX, BOD, COD, TOC, color and turbidity. Several of these parameters are proportional to the amount of lignin that is removed during the bleaching process [13,24,25]. It is important to characterize the residual lignin of high-kappa, high-yield pulps, as well as the dissolved organics generated during bleaching, in order to develop effective wastewater treatment methods to eliminate these components. If such treatment methods can be developed, it may allow for higher yield pulping techniques to be accepted by the industry.

This study characterized the organic material from the ECF bleaching of a high-yield hardwood kraft pulp in terms of structural groups and molecular weight distributions of the dissolved organics. By defining the organic structures in the effluents, it is hoped that future research efforts can specifically reduce/eliminate these components prior to wastewater treatment.

MATERIAL AND METHODS

Wood

Mixed-species hardwood chips (with less than 5% pine contamination) were provided by a WestRock mill (Covington, VA, USA). Knots and bark were removed from the mill chips prior to their characterization and to kraft pulping. Sorted chips were ground in a Wiley mill and sieved; the fraction retained between 40 and 60 mesh screens was collected. The milled wood was extracted in a Soxhlet apparatus for 24 h using a benzene-ethanol mixture (2:1 v/v ratio) (TAPPI Standard Test Method T 264 om-88 “Preparation of wood for chemical analysis”). Carbohydrate and Klason lignin analyses were determined by the methods prescribed by Theander and Westerlund [26], and by TAPPI Test Method T 222 om-06 “Acid-insoluble lignin in wood and pulp,” respectively. Acid soluble lignin was measured on the acid hydrolysate obtained from the Klason analysis using TAPPI Useful Method UM 250 “Acid-soluble lignin in wood and pulp.”

Cellulolytic enzyme lignin (CEL)

Extractive-free sawdust (2 g) was milled in a planetary ball mill (Pulverisette 7, Fritsch; Idar, Oberstein, Germany) for 6 h. The mill was operated at 600 rpm using 17 zirconium dioxide (ZrO_2) balls. The meal was then treated with cellulase (Novozymes CTec2, Novozymes; Bagsvaerd, Denmark) and hemicellulase (Novozymes HTec2) in a ratio of 9:1 (v/v) cellulase-to-hemicellulase. The enzymatic treatment was conducted in a 4.8 pH sodium acetate buffer at 50°C and 5% consistency. The enzyme loading was 10 FPU/g, and the hydrolysis treatment time was 72 h. The hydrolyzed mixture was centrifuged and decanted, and the resulting solids were treated to a second round of enzyme addition using the same conditions as described for the first treatment. Afterwards, the hydrolyzed material was centrifuged to obtain the solids. The solid phase was collected, washed thoroughly with deionized water, and freeze dried. The dried material was extracted with a p-dioxane/water medium (96:4 v/v ratio). After extraction, the medium was evaporated under a vacuum at 40°C to yield the solid cellulolytic enzyme lignin (CEL).

Kraft pulping

Kraft pulping experiments were performed in a 10-L M/K laboratory digester (M/K Systems; Elk Grove Village, IL, USA) equipped with temperature controller, liquor recirculation, and an indirect heating system. The general cooking conditions are shown in **Table I**. Batch cooks were performed using 1000 g oven-dried (o.d.) hardwood mill chips with knots and bark removed. Pulped chips were placed in a stainless-steel box with a 150-mesh screen, washed thoroughly with water, and disintegrated. The washed pulp was centrifuged to approximately 30% consistency and was subsequently stored in polyethylene bags. Pulp yield and kappa number were determined by gravimetric methods and by TAPPI Test Method T 236 om-06 “Kappa number of pulp,” respectively.

Parameter	Conditions
Temperature	168°C
H-factor	800
Sulfidity	34%
Active alkali	18%
Liquid/Wood ratio	4:1
Kappa number	26
Pulping yield	51%

I. Kraft pulping.

Bleaching

Oxygen delignification

The unbleached kraft pulp was subjected to oxygen delignification (O-stage) performed in a pressurized vessel. The vessel was preheated to 70°C–80°C. The heated vessel was loaded with 200 g pulp (o.d.) and 2% sodium hydroxide (NaOH) (on pulp); the consistency was adjusted to 10% with distilled water. The vessel was pressurized with oxygen at 100 psig, and then placed in a 110°C hot air oven. After 60 min reaction, the vessel was placed into a cold-water bath and depressurized. The pulp was washed, centrifuged to approximately 30% consistency, and stored in polyethylene bags. The kappa number of the hardwood kraft pulp after oxygen delignification was 14.2.

Chlorine dioxide delignification

Chlorine dioxide delignification (D_0 stage) was performed in polyethylene bags. A 0.24 kappa factor charge was used in the D_0 stage. Oxygen-delignified pulp, bleach liquor, and distilled water were manually mixed in the bag at 10% consistency and room temperature. The bag was placed in a 70°C water bath for 60 min. At the end of the reaction, D_0 filtrates were collected for analyses. The resulting D_0 pulp was washed, centrifuged to approximately 30% consistency, and stored in polyethylene bags. The kappa number of the OD_0 pulp was 5.8.

Alkaline extraction

Alkaline extraction (E stage) was performed in polyethylene bags. Extractions were conducted on D_0 -treated pulps at 10% consistency, 70°C, and 60 min using 2% NaOH (on pulp). Deionized water containing NaOH was manually mixed with the pulp in a bag at room temperature. Subsequently, the bag was placed into a preheated water bath for the prescribed temperature and reaction time. At the end of the reaction, E filtrates samples were extracted for analyses. The resulting pulp was washed, centrifuged to approximately 30% consistency, and stored in polyethylene bags. The kappa number of the OD_0E pulp was 5.0.

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Bleaching effluents analyses

Gel permeation chromatography (GPC)

The bleaching effluents were vacuum dried and subjected to molecular weight distribution analysis using gel permeation chromatography (GPC). The GPC system (Shimadzu; Kyoto, Japan) consisted of an LC-20AD pump, a CTO-20A oven that was equipped with HR 1 and HR 5E styragel columns (Waters; Milford, MA, USA), and an SPD-20A UV/Vis detector and a RID-10A reflective index (RI) detector connected in series. The oven temperature was set to 35°C. The UV/Vis detector used dual wavelength set to 235 nm and 280 nm. The mobile phase used was an aqueous tetrahydrofuran solution (5 mg/L), which flowed at a rate of 0.7 ml/min. A calibration curve for estimating molecular weight distributions was generated using twelve polystyrene standards (PSS ReadyCal-Kit, Polymer Standards Service; Mainz, Germany).

Nuclear magnetic resonance (NMR) spectroscopy and two-dimensional heteronuclear single quantum coherence (2D HSQC)

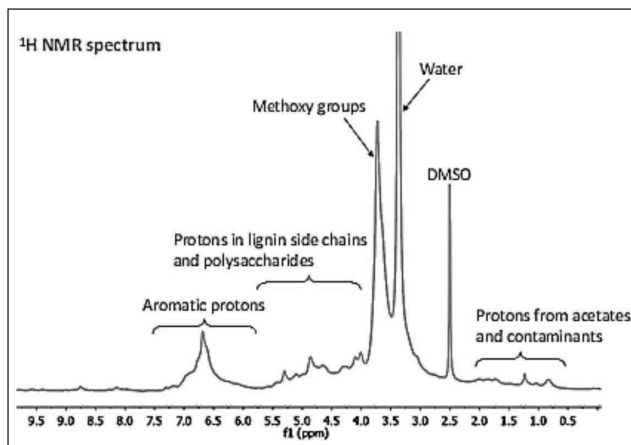
Two-dimensional (2D) proton (1H) and carbon-13 (13C) heteronuclear single quantum coherence (HSQC) correlation NMR spectra were acquired according to the procedures described by Capanema et al. [27]. The samples were dissolved in dimethyl sulfoxide-d₆ (99.9%; VWR; Radnor, PA, USA) at ca. 20% concentration. The 2D HSQC NMR spectra were acquired on a Bruker AVANCE 500 MHz spectrometer (Bruker; Billerica, MA, USA) equipped with a 5-mm double resonance broadband BBI inverse probe using a coupling constant 1J_{C-H} of 147 Hz.

RESULTS AND DISCUSSION

Monosaccharide and lignin characterizations

Table II shows the major constituents of the hardwood chips used in the pulping experiments. Table II includes extractives, monosaccharides of the carbohydrates, Klason lignin, and acid-soluble lignin. These wood chips were used to perform lignin isolation analyses, kraft pulping, and kraft pulp bleaching.

It is important to characterize the lignin in the wood chips before and after kraft pulping, as well as during the bleach sequence, in order to understand how this component is altered. For a better understanding of the functional features of lignin, a lignin-rich sample was prepared by removing most of the carbohydrates by enzymatic hydrolysis. The lignin content of the hydrolyzed CEL residue was greater than 90%. NMR techniques (1H NMR and 2D HSQC NMR) were used to



2. The proton nuclear magnetic resonance (1H NMR) spectrum of the lignin-rich (cellulolytic enzyme lignin [CEL]) sample from hardwood chips.

characterize the CEL, and the results are shown in **Fig. 2** and **Fig. 3**.

The 1H NMR of the lignin-rich (CEL) spectrum is shown in Fig. 2; however, some of the signal peaks from the lignin overlapped with signal peaks from the carbohydrate contaminants. These peaks can be deconvoluted by using 2D HSQC NMR (Fig. 3). The major lignin signals in the 2D HSQC NMR spectrum are from β -O-4' linkages, phenylcoumaran, resinol, methoxyl groups, guaiacyl units, syringyl units, oxidized syringyl units, and side chains of cinnamyl alcohol groups. Some of these detected structural features of lignin are depicted in **Fig. 4**.

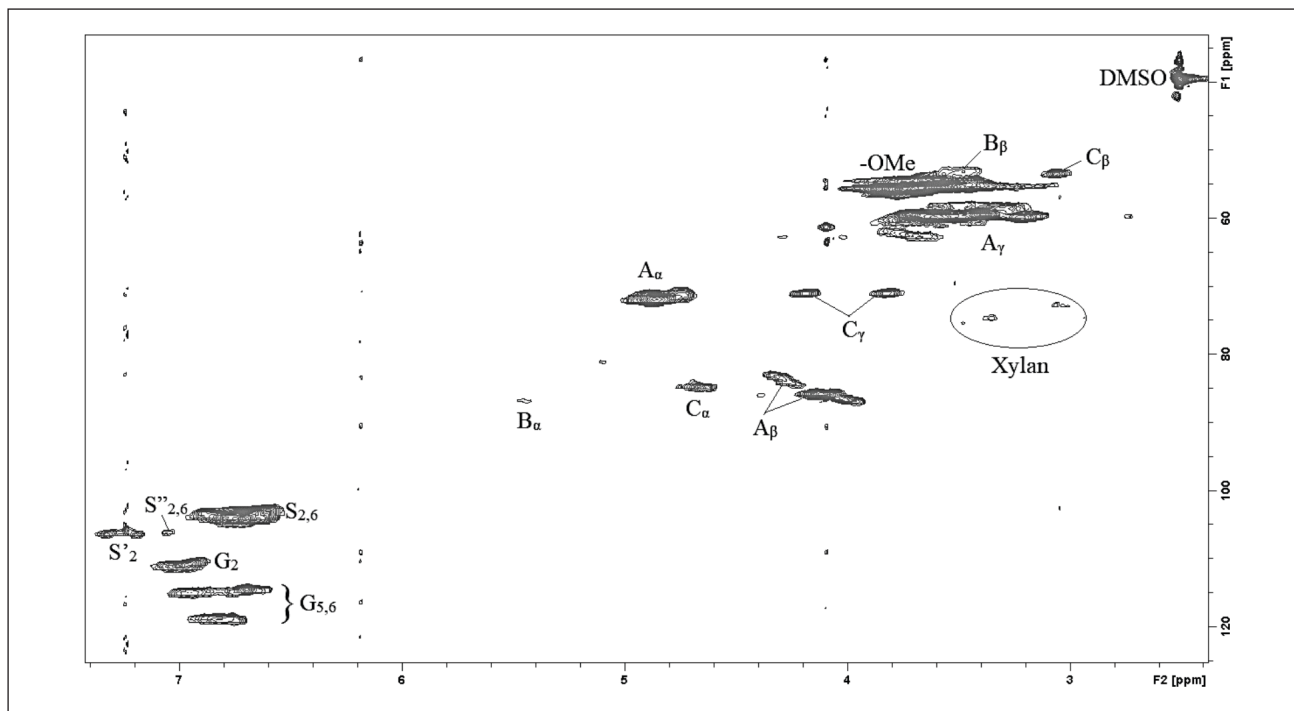
According to Stevanovic [28], the β -O-4' (arylglycerol- β -aryl) ether bond is the most common structural feature found in protolignin regardless of the lignocellulose source (i.e., softwoods, hardwoods, or grasses). This structural feature comprises 40% to 60% of the linkages between the phenylpropane units. Similar observations are noted with the isolated CEL in this study. Stevanovic [28] also notes other prominent substructure features such as: phenylcoumaran (β -5); carbon-carbon linkages like biphenyl (5-5'); β - β (side chains); and 1,2-diarylpropane (β -1); diaryl ether (4-O-5'); benzyl aryl ether (β -O-4'); conjugated carbonyl groups; cinnamyl alcohol groups; and carboxylic groups.

Bleaching effluents characterization

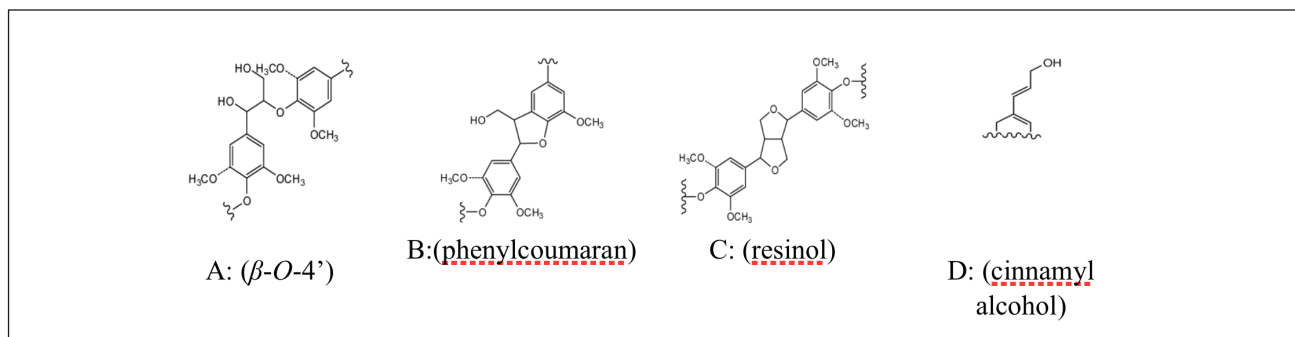
The wood chips were subjected to kraft pulping, which was followed by oxygen delignification (O), chlorine dioxide delignification (D₀), and alkaline extraction (E). After each stage,

Extractives, %	Glucan, %	Xylan, %	Mannan, %	Galactan, %	Klason Lignin, %	Acid-Soluble Lignin, %
4.1	36.2	14.6	4.5	1.4	27.2	3.8

II. Composition analysis of wood sample.



3. The two-dimensional heteronuclear single quantum coherence (2D HSQC) NMR spectrum of lignin-rich (CEL) sample from hardwood chips. (G: guaiacyl units; S: syringyl units; and S' and S'': oxidized syringyl units. A, B, C and D refer to lignin substructures in Fig. 4).



4. Major lignin substructures detected by 2D HSQC NMR.

the bleach filtrates were collected and analyzed by GPC and by NMR spectroscopy to characterize the molecular weight distributions and functional groups, respectively, of the dissolved organics.

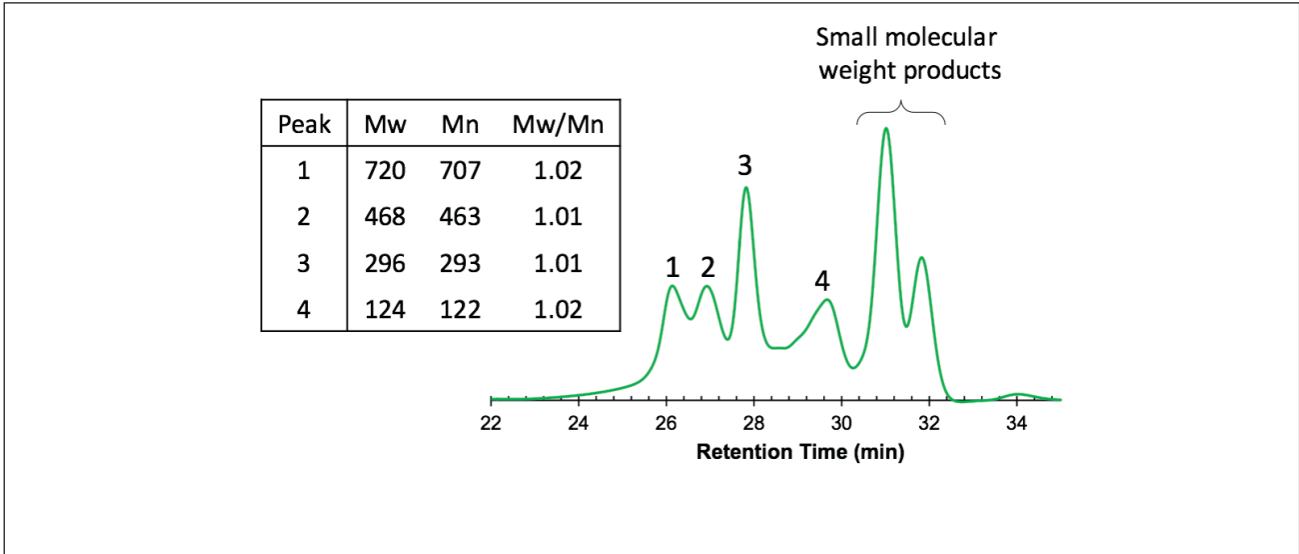
Molecular weight distribution (MWD)

The GPC analyses of the bleaching effluents are shown in **Fig. 5**, where the eluted peaks were detected by refractive index (RI). The O-stage filtrate had a number average molecular weight (M_n) of 299, a weight average molecular weight (M_w) of 919, and a polydispersity index (M_w/M_n) of approximately 3. These observations indicated that the MWD of this effluent was broad. The D_0 -stage effluent had lower values of M_n (264) and M_w (470), as well as the polydispersity index (1.78), when compared to the O-stage filtrate.

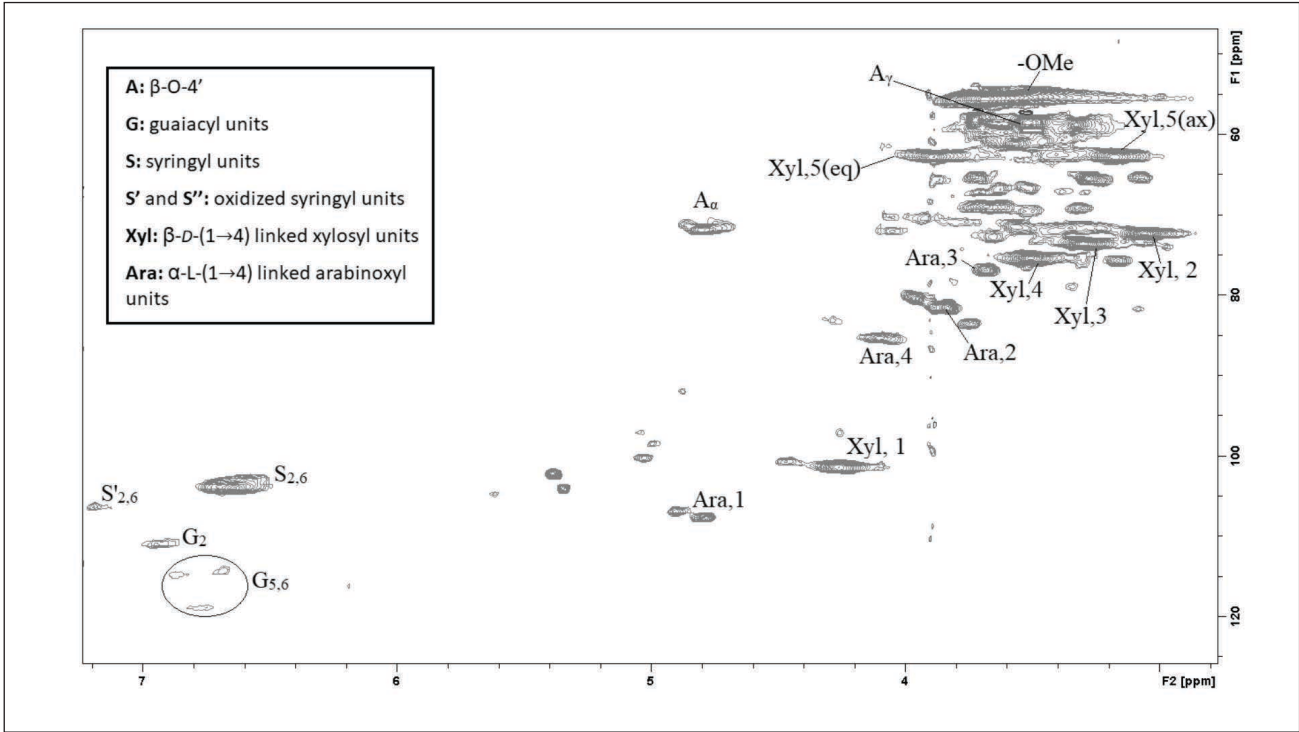
Generally, the purpose of the E stage is to remove colored

and oxidized components of the D_0 treated pulp. This organic material is ionized and solubilized in the warm alkali liquor of the E stage. Its removal from OD_0 pulp results in a decrease in bleaching chemical demand in subsequent brightening stages [29]. Several large molecular weight elution peaks were observed for the E-stage effluent (Fig. 5c) when compared to the D_0 -stage effluent, which is probably due to the improved solubility of the high molecular weight material in alkaline versus acidic environments.

Biological treatment systems tend to remove low molecular weight organics with high efficiency. On the other hand, higher molecular weight organics tend to be recalcitrant towards biological treatment [30]. These components, typically derived from lignin, tend to be hydrophobic in nature. Hydrophilic organic constituents generally have lower molecular weights and are often derived from heavy-modified lignin



5. Molecular weight distribution of effluent components recovered from the O stage;. Elution GPC detected by refractive index (RI).



6. The 2D HSQC NMR spectrum of oxygen delignification (O-stage) effluent.

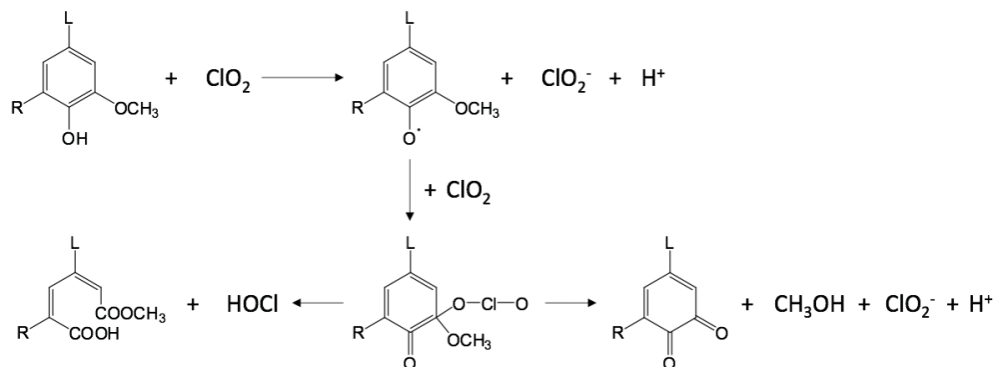
fragments and from solubilized carbohydrates, hemicelluloses, and protein-like materials [31].

Nuclear magnetic resonance (NMR) spectroscopy

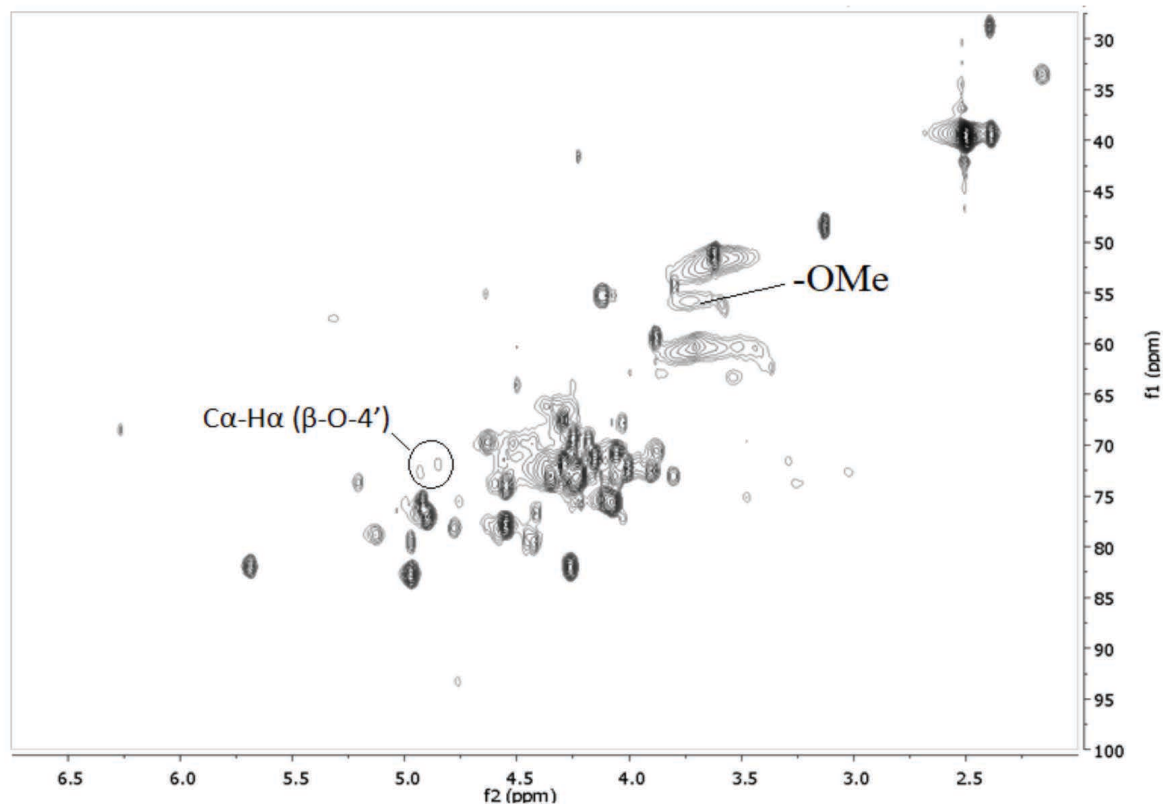
Oxygen delignification

The O stage removes residual lignin in the kraft brownstock to lower the demand of oxidants in subsequent bleaching stages. This stage is often considered an extension of the kraft pulping, which lowers the kappa number of the pulp by 25%

to 65% [32]. The efficiency of oxygen delignification can be seen when analyzing the 2D HSQC NMR spectrum of the O-stage effluent (**Fig. 6**). A substantial amount of lignin signals in the effluent was detected from the aliphatic side chains and the aromatic rings. Moreover, strong xylan signals were observed. It is possible that the carbohydrate material is from xyans that are covalent bonded to lignin (i.e., lignin-carbohydrate complexes [LCCs]) or these signals could have resulted from precipitated xylan from the end of the kraft cook being



7. Common reactions between phenolic lignin and chlorine dioxide during the D_0 stage generating olefinic and carbonyl functional groups.



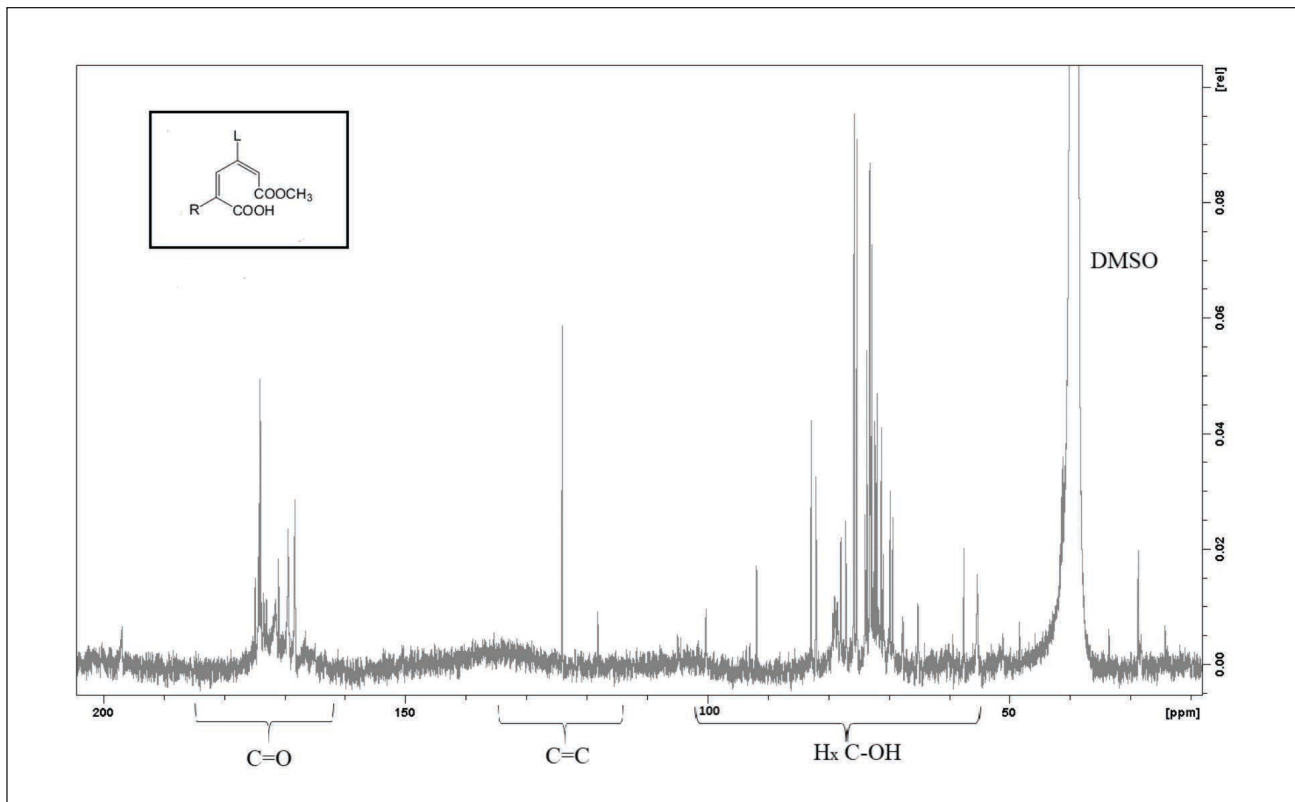
8. The 2D HSQC NMR spectrum of chlorine dioxide delignification (D_0 -stage) effluent.

resolubilized during the oxygen delignification stage. A study performed by Balakshin et al., which used advanced 2D HSQC techniques with a high-resolution NMR (950 MHz), has identified and reported the presence of LCCs in milled-wood lignin and CELs isolated from birch and pine wood samples [33]. On the other hand, it is possible that this material was derived from the re-precipitation of xylans on the fibers towards the end of kraft pulping [33,34]. Redeposited xylan can be re-

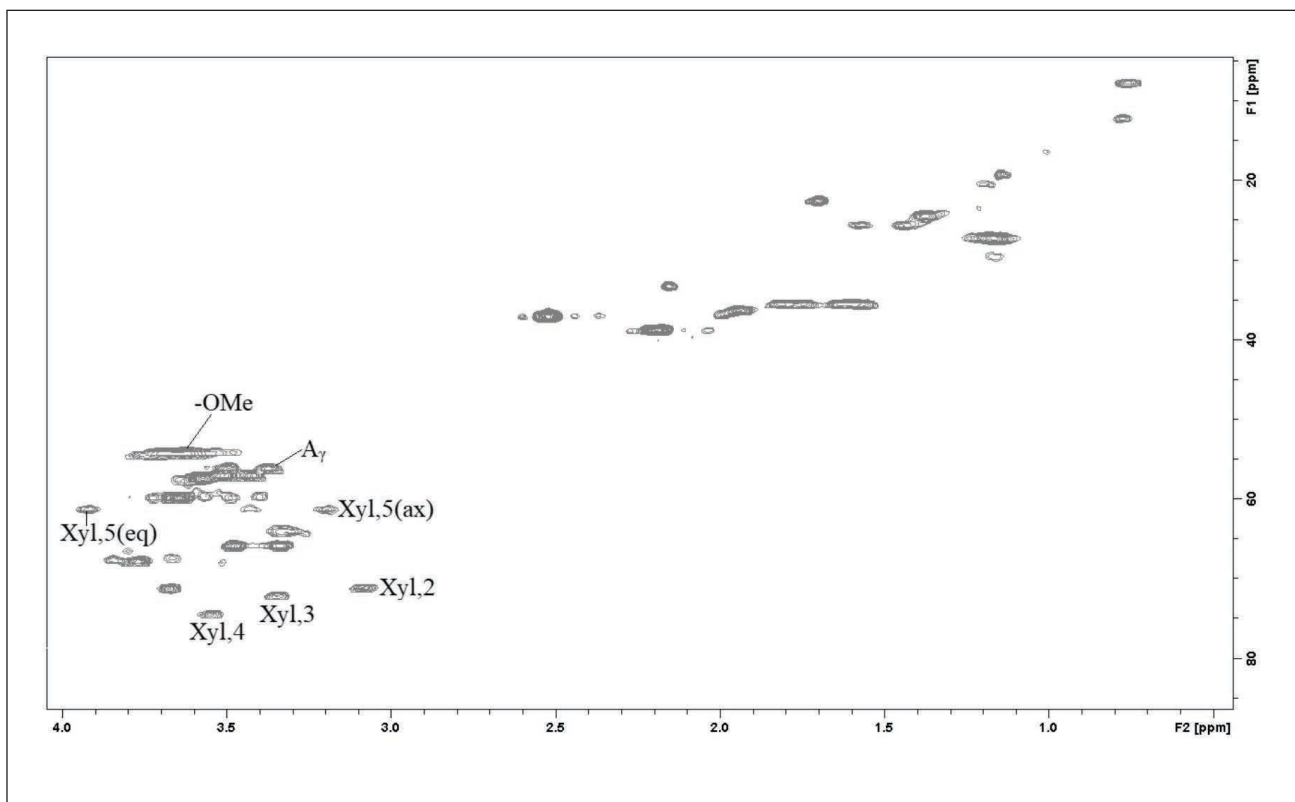
solubilized in the alkaline liquor while undergoing oxygen delignification. Hence, the oxygen delignification may not have only removed substantial amounts of kraft lignin from the pulp, but also removed some redeposited xylans from the fiber surface.

Chlorine dioxide delignification

The wide spread use of chlorine dioxide delignification can



9. The carbon-13 nuclear magnetic resonance (^{13}C NMR) spectrum of chlorine dioxide delignification (D_0 -stage) effluent.



10. The 2D HSQC NMR spectrum of alkaline extraction (E -stage) effluent.

be attributed to its high selectivity to oxidize and fragment the residual kraft lignin while preserving carbohydrates and pulp strength [29]. The main reaction occurring is lignin oxidation and removal. **Figure 7** depicts some common reactions of chlorine dioxide with reactive phenolic groups in the kraft residual lignin.

The 2D HSQC NMR spectrum of the D₀ effluent, unlike the O effluent, contained fewer signals corresponding to unmodified lignin and to carbohydrate functional groups. Only two weak NMR signal peaks were detected. One is assigned to the methoxyl groups. The other signal is from the C_α position of β-O-4' linkages (**Fig. 8**). There were many other signals detected that likely originated from low molecular weight compounds (i.e., highly degraded organics). This observation suggests that the aromatic structure of the lignin was oxidized and degraded by chlorine dioxide.

The effectiveness of the D₀ stage can also be observed in the ¹³C NMR spectrum of the D₀ effluent (**Fig. 9**). The spectrum showed that ring opening reactions occurred with the aromatic nuclei, and that there were no obvious aromatic carbon peaks. Aromatic compounds would result in broad peaks from 102 to 162 ppm. The D₀ effluent showed relatively few peaks in this region. Instead, peaks were found in the range of 120 to 130 ppm and at 165 to 170 ppm. These peaks are believed to originate from olefinic (C=C) and carbonyl (C=O) groups of highly-oxidized kraft lignin (e.g., muconic type structures).

Alkaline extraction

The E stage is conducted in order to solubilize the oxidized lignin generated from the D₀ stage. As was noted with GPC analyses, the E-stage effluent contained larger molecular weight organics (**Fig. 5c**) than the effluent from the D₀ stage (**Fig. 5b**). The 2D HSQC NMR analyses of the E-stage effluent showed the presence of several lignin structural features that were not noted in the D₀-stage effluent (**Fig. 10**), such as the Cγ position of β-O-4' linkages (A_γ).

CONCLUSIONS

The major features found in the cellulolytic enzyme lignin (CEL) from hardwood chips were β-O-4' linkages, phenylcoumaran structures, resinol structures, methoxyl groups, guaiacyl units, syringyl units, oxidized syringyl units, and side chains of cinnamyl alcohol. The molecular weight distribution (MWD) of the effluent from oxygen delignification is broader than the MWDs of effluents from the D₀ and E stages. Moreover, the O-stage effluent contained high amounts of lignin fragments and dissolved xylan. The 2D HSQC NMR spectra indicated that oxygen delignification has a high effectiveness in removing kraft residual lignin and xyans. Also, the effluent from the D₀ stage, unlike the O stage, contained lower amounts of dissolved fragments with high molecular weight and higher amounts of dissolved fragments with low molecular weight. Furthermore, it was noted that the D₀ effluent was

deficient of aromatic carbon peaks in the ¹³C NMR spectrum, whereas peaks for olefinic (C=C) and carbonyl (C=O) functional groups were present. These observations suggested that the dissolved lignin from chlorine dioxide delignification was highly degraded and modified. Finally, the dissolved organics found in the E-stage effluent were higher in average molecular weight than those from the D₀ stage; this observation was attributed to the ionization and solubilization of D₀-stage oxidized lignin in an alkaline environment. **TJ**

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ABOUT THE AUTHORS

We developed a pulping process that substantially enhanced pulp yield. One problem with this process is an increase in organics generated in the bleach plant. We wanted to understand the components of these materials as a first step in reducing or destroying them prior to release into the waste treatment plant.

Several bleach plant characterization studies have been conducted on chlorine-based bleaching sequences. However, only limited studies have been performed on elemental chlorine free (ECF) bleaching effluents and almost none on higher kappa number pulps in an ECF bleaching sequence.

A significant number of complex analytical tests had to be performed in this study, and obtaining quantifiable results required rigorous lab techniques. It was very interesting to find that aromatic structures were nearly absent in the D₀-stage filtrate.

The results indicated that the molecular weight distribution (MWD) of the dissolved organics from oxygen delignification effluent is broader than those from D₀- and E-stage effluents.

The current work is a first step in understanding the composition of these effluent streams. Further research and development efforts will be required to develop improved treatment methodologies.



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Du



Hart



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