

Salient Reactions in Lignin During Pulping and Oxygen Bleaching: An Overview

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This overview attempts to summarize our efforts focussed on defining the formation of the various condensed structures in lignin as they emerge during conventional kraft, EMCC, soda and oxygen-delignification conditions. The role and fate of the newly discovered structures of dibenzodioxocins are also discussed and their significance toward pulping and bleaching operations emphasized. Finally, the fate and role of the condensed phenolic and p-hydroxyphenyl structures under oxygen-delignification conditions are discussed.

Nous résumons ici notre travail visant à définir la formation de diverses structures condensées de lignines développées lors de la délignification à l'oxygène, du procédé EMCC, et de la cuisson kraft classique et à la soude. Nous discutons aussi du rôle et du sort des oxanthrènes (dibenzodioxocines) et mettons l'accent sur leur signification lors de la mise en pâte et du blanchiment. Nous discutons aussi du sort et du rôle des structures p-hydroxyphényles et phénoliques condensées lors de la délignification à l'oxygène.

INTRODUCTION

While the ether bonds of lignin cleave efficiently under alkaline pulping conditions, the formation of condensed structures decrease its reactivity and diminish the solubility of residual lignin from within the pulp matrix. During the past several years, a number of modifications have been proposed for the conventional kraft pulping process, aimed at enhancing delignification. Rapid displacement heating and modified continuous cooking are two examples of these processes. Among the reactions that are known to interfere with the process of alkaline delignification are those involving the formation of carbon-carbon bonds.

On another front, regulatory and economic pressures have driven the pulp and paper industry to implement new delignification and bleaching practices. A major transition is the partial replacement of chlorine or chlorine dioxide delignification stages with oxygen delignification. However, the effectiveness of an oxygen-delignification stage is limited to the 50% level. Beyond this level, severe cellulose degradation takes place, resulting in the deterioration of pulp viscosity and strength charac-

teristics. This selectivity issue is a major drawback of oxygen delignification.

Aromatic condensation reactions also have been thought to decrease the reactivity of residual lignin toward oxygen delignification [1,2]. The reactivity of various condensed units present in kraft pulp has been explored using degradation techniques. Condensed structures such as diphenylmethane (DPM) and biphenyls were found to be resistant during oxygen delignification and were held responsible for the slow phase of oxygen delignification [1,3]. The reactivity of the condensed structures within residual kraft lignin under oxygen-delignification conditions was recently evaluated in detail [4,5]. Even under homogeneous oxidative conditions with no mass-transfer limitations operating, the 5-5' biphenyl condensed structures were found to be fairly stable toward the oxidation [5]. Despite the many research efforts, the question of which structures are responsible for activation and which are responsible for lignin deactivation during oxygen delignification still remain unanswered. In view of the above, we focussed our efforts on defining the formation of DPM and 5-5' biphenolic structures in lignin as they occur during conventional kraft and soda pulping conditions [6]. The accumulated kinetic data for the formation of these species under soda and kraft pulping conditions was then correlated to known chemistry [6]. Furthermore, our continuing efforts to understand the fundamen-

tals of oxygen delignification prompted us to focus on systematically examining the residual lignins within an oxygen-delignified fibre [7]. To do this, a newly developed method for isolating residual lignin [8], which provides residual lignin in high yield, was coupled with a systematic sampling of delignified pulp and spent liquor at various stages of oxygen delignification. The isolated residual and solubilized lignins were then subjected to detailed spectroscopic analyses [8,9]. This approach allowed a systematic assessment of the structural changes occurring within the lignin during the oxidation process. This paper will attempt to summarize our findings in this important area.

EXPERIMENTAL

Details of the experimental procedures discussed in this overview have already appeared in the literature [4-11]. More specifically, the details of treating milled-wood lignin under homogeneous kraft or soda pulping conditions are given in [6]; while the details of the oxygen-delignification experiments dealing with lignin samples isolated from fibres are given in [7]. The new residual lignin isolation protocol applied during the overall effort described in this paper has been published in [8], while the novel quantitative ¹³C nuclear magnetic resonance (NMR) spectroscopic acquisition protocol using internal standards is described in detail in [9]. Traditional

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quantitative ^{31}P NMR spectra were acquired using the methods described in [10,11]. Residual lignins isolated according to the method described in reference [8] were also fragmented by derivatization followed by reductive cleavage (DFRC), as described in detail in [12]. The fragmented lignins were then subjected to alkaline hydrolysis (0.2 mol/L NaOH, 50°C, 24 h) and dialyzed for 105 h against 0.2 mol/L NaOH using a conventional dialysis membrane with a

molecular weight cutoff limit of ~1000 g/mol. The acidified (pH 2) dialyzates were then subjected to silylation followed by qualitative gas chromatography/mass spectrometry (GC/MS) measurements using the methods and GC/MS acquisition protocol described in [4]. Analytical pyrolysis measurements were carried out in accordance with the methods described in [13,14].

RESULTS AND DISCUSSION

Lignin Condensation Reactions during Pulping

In our earlier work, the phosphorus NMR spectra of solubilized kraft lignin contained a signal, among others, centred around 143.5 ppm [10]. On the basis of model compound work and calculations based on the Hammett prin-

ciples [11], this signal was assigned to be due to diarylmethane structures possessing free phenolic hydroxyl groups [11]. In an effort to further substantiate our conclusions, we then carried out two series of isothermal (120°C) kraft and soda pulping experiments followed by quantitative determinations of the DPM structures and correlated our findings with the differences in chemistry known to occur between the two processes [6]. The data of Table I clearly demonstrate that the formation of DPM structures is a considerably more facile reaction under soda pulping conditions than under kraft pulping conditions. Sulphide ions present in kraft liquors are responsible for promoting and accelerating lignin fragmentation reactions as well as suppressing undesirable condensation reactions [1,15-18].

The presence of sulphide ions within sulphate liquors has been believed to preclude the liberation of formaldehyde from the lignin biopolymer [17]. Alternatively, the absence of sulphide, i.e. soda pulping, allows the intermediate quinone methides to lose formaldehyde, causing the formation of undesirable alkaline stable enol ethers [18,19]. The rate data of Table I clearly demonstrate the efficiency of formation of diphenylmethanes under soda pulping conditions, especially early in the process. Therefore, it is not surprising that bleaching a soda-AQ pulp is more difficult than bleaching a kraft pulp of a similar kappa number [20] (Fig. 1).

In an effort to substantiate further our conclusions pertaining to the presence of DPM structures in residual lignins, we isolated residual lignins from a kraft pulp of kappa no. 28 according to the method described in [8]. This material was then subjected to a selective degradation scheme to further depolymerize it, i.e. DFRC, as described in detail in [12]. Dialyzates of the fragmented lignins were then subjected to qualitative GC/MS measurements. The resulting chromatograms representative of the dimer region of the chromatograms shown in Fig. 1 show a significant number of dimeric compounds that up to now have been believed to exist only in black liquors. Of particular significance to the present discussion are compound 5 of Fig. 1A and compound 1 of Fig. 1B, indicating the DPM linkage, providing unequivocal evidence for the presence of such structures within residual kraft lignin, albeit in relatively minor proportions. Another structure of significance to kraft pulping is the isolation of the dithiane 2 (Fig. 1B). These structures are thought to form at lower pulping temperatures during the kraft process via dimerization reactions of the open form of the episulphide intermediate (Fig. 2).

On the Abundance of Dibenzodioxocins in Lignin

In 1995, Brunow's group [21,22] announced the discovery of the dibenzodioxocins bonding patterns as being prevalent in softwood lignins. This involves the formation of α, β ethers on the same 5-5' biphenyl structure (Fig. 3).

In fact, the presence of these structures

Reaction Time (min)	Diphenyl Methane Structures x 10 ⁴ (mol/g)	
	Kraft Pulping	Soda Pulping
60	0.83	1.60
120	1.41	2.20
180	2.41	3.10
240	4.10	4.30

1. Milled-wood lignin (softwood, *Picea mariana*).
2. Amount of sodium sulphide was replaced with sodium hydroxide.
3. The temperature of the pulping experiments was set at 120°C.

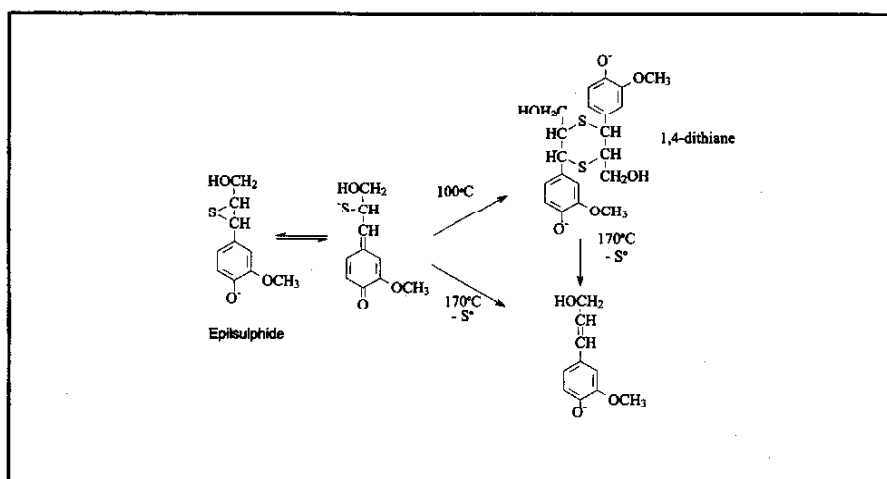


Fig. 2. Reactions of the episulphide intermediate thought to occur in kraft pulping causing the formation of the detected 1,4-dithiane (2) shown in Fig. 1B.

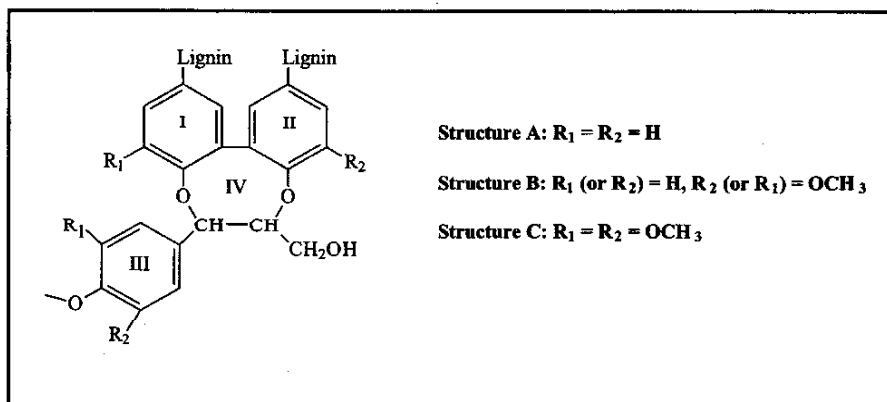


Fig. 3. The dibenzodioxocin structures present in lignins. For poplar lignins, it is anticipated that all structures, A, B, C are present while, for spruce, the structure C predominates.

in lignins now provides a plausible branching point, accounting for its crosslinked nature. The new octagonal fragment, when subjected to soda pulping conditions, was shown to release significant amounts of structures bearing 5-5' biphenolic hydroxyl groups [21]. Therefore, under kraft pulping conditions, it is likely that similar reactions will occur, releasing 5-5' biphenolic hydroxyl groups. In an effort to determine these structures, we carried out a series of kraft cooks on samples of isolated milled-wood lignins and then determined the amount of liberated 5-5' biphenols using quantitative ^{31}P NMR [23]. The data from this effort showed that, indeed, such structures are released in very significant amounts under kraft pulping conditions (0.4 mmol/g). Assuming that all the released 5-5' biphenols belong to dibenzodioxocins, then, within 100 phenyl propanoids in lignin, about 10 of them are involved in dibenzodioxocin formation. Since 3 phenyl propane units are involved in one dibenzodioxocin structure, one may express this value as 3.5–4.0 dibenzodioxocin rings per 100 C_9 units. This important conclusion was independently confirmed using a different lignin degradation protocol based on DFRC [12,23] and subsequent detailed ^{31}P NMR and quantitative 2-dimensional NMR measurements on milled-wood lignin [24]. When coupling the information derived from the estimation of the amount of dibenzodioxocins in softwood lignins [2] with the understanding of the reactivity of residual lignin under oxygen-delignification conditions [4,7], one realizes that such lignins contain very significant amounts of 5-5' biphenolic character. The chromatographic data of Fig. 1B supply additional evidence pertaining to the significance of this conclusion. Compound 3, identified in the dialyzate of residual kraft lignin, is seen to be present in significant abundance within the dimer region of the chromatogram. Current efforts in our laboratory pertain to understanding the reactivity of the 5-5' moieties and its significance in controlling brightness in the bleach plant.

Lignin Condensation Reactions during Oxygen Delignification

In our earlier work, we demonstrated

that, under homogeneous oxidative conditions, the rate of elimination of condensed phenolic units in residual kraft lignin was slower than the rate of elimination of uncondensed guaiacyl phenolic units [5]. Of the condensed structures, 5-5' biphenolic structures showed the highest oxidative resistance. They decreased in the initial phase of oxidation but, after ~40 min of treatment, their content did not decrease further. This resulted in a significant accumulation of the condensed hydroxyls content within the oxidized residual lignin. Consequently, and in light of the previous discussion on dibenzodioxocins, we have paid particular attention to the behaviour of the condensed phenolic structures, and more specifically to the development of 5-5' biphenyl structures within the residual lignins as a function of the intensity of oxygen delignification [7]. Within the solubilized lignins, the condensed phenolic OH content was found to decrease by ~25–30% during the initial stages of delignification (20 min) and then remained essentially constant. In the residual lignins, however, the 5-5' biphenolic condensed structures were found to decrease from 0.44 to 0.38 mmol/g during the early phases of oxygen delignification, and then started to build up again to a value of 0.49 mmol/g. However, when the liquor coexisting with the pulp was replaced in a series of multistage experiments, the content of 5-5' biphenyls did not increase. Even after a prolonged three-stage delignification, the level of 5-5' hydroxyls remained at 0.44 mmol/g; that is lower than the 0.49 mmol/g level reached in the corresponding one-stage oxygen delignification. The observed increase of 5-5' biphenyl hydroxyls could be attributed to secondary condensation reactions. Such reactions, which most likely occur between phenoxy radicals forming on the mobile solubilized fraction and the radicals forming on immobilized residual lignin, generate new 5-5' condensed structures.

In an effort to further support our measurements of 5-5' biphenolic structures, we measured them using an independent method. Having developed a quantitative ^{13}C NMR protocol [9] (using an internal standard), we were able to measure the precise amounts of 5-5' biphenyl fragments and their development within residual oxidized lignins as a function of

the extent of oxidation. These data showed that the content of etherified 5-5' biphenyl structures after 80 min increased over the overall time scale of the oxidation (Fig. 4). The inert nature of such structures under oxygen-delignification conditions could be held responsible for this enrichment.

These observations correlate well with earlier experiments attempting to understand the mechanism of oxygen delignification, using isolated residual kraft lignin oxidized under homogeneous conditions [4,5]. These accounts, coupled with the present findings, support the idea that the 5-5' biphenolic structures are unreactive under oxygen-delignification conditions. The accumulation of these groups during oxygen delignification could be another factor imposing limits to the process while the role of lignin-carbohydrate linkages still remains unclear.

Accumulation of p-Hydroxyphenyl Units

A comparison of the hetero multiple-quantum coherence (one-bond ^{13}C - ^1H correlation technique, which displays the signals of carbon atoms directly linked to protons) NMR spectra of the initial residual lignin and the sample isolated after 80 min of delignification [7] revealed that a new group of signals appeared in the spectra of the oxidized lignin. These signals appear in the downfield region assigned to aromatic nuclei characteristic of p-hydroxyphenyl structures [25]. In the spectrum of residual kraft lignin before oxidation, the p-hydroxyphenyl signals were below the detection limit and could not be identified. To further confirm and quantify the presence of these structures within the residual lignin, we examined the quantitative ^{31}P NMR spectra of the isolated residual lignins. The p-hydroxyphenyl OH gives rise to a well resolved peak at 137.8 ppm in the spectra of the oxidized lignin [26]. As such their amount within the residual lignin was quantified and was shown to progressively increase by more than threefold during oxygen delignification (from 0.04 mmol/g at 0 min to 0.15 mmol/g at 160 min [7] (Fig. 5)). When the content of these structures was calculated on a per gram of pulp basis, it was found that their content remained essentially constant

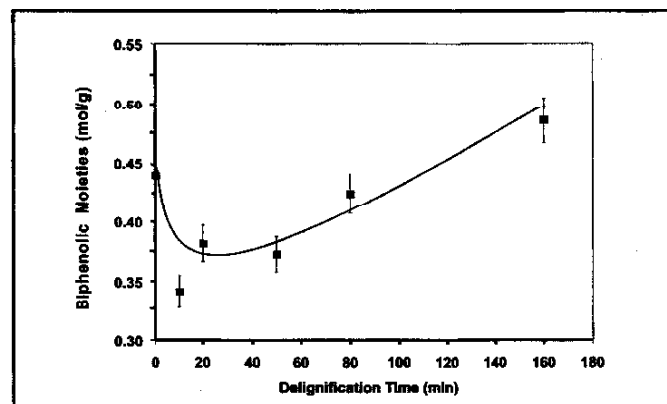


Fig. 4. 5-5' Biphenyl structures present within the residual lignin at various points along a conventional oxygen-delignification process.

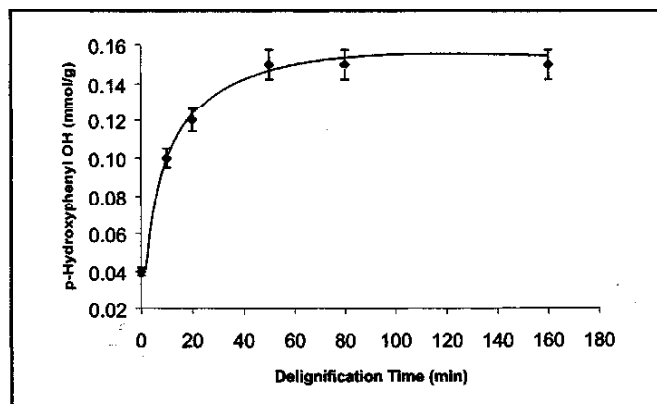


Fig. 5. p-Hydroxyphenyl OH content in the residual lignin at various points along a conventional oxygen-delignification process.

throughout the delignification process. This clearly indicates that these units accumulate and do not form during oxygen delignification.

To further validate these conclusions, a series of isolated residual lignin samples was subjected to further analyses using a combination of analytical pyrolysis coupled to a gas chromatographic and a mass spectroscopic detector (Py-GC-MS). The results in Table II show that the relative content of p-hydroxyphenyl units within the pyrolysis products increased with increasing delignification time. Since three independent analytical techniques corroborate the presence and accumulation of such units within the oxygen-delignified pulp, this represents convincing evidence for their presence and role in the process.

Softwood lignin contains small amounts of p-hydroxyphenyl units. Estimates for their abundance vary from 5% (*Picea abies* [27]) to 13% (*Pinus taeda* [28]). If p-hydroxyphenyl units survive oxygen delignification, or at least undergo only limited degradation compared to the guaiacyl units, such structures may accumulate within the residual lignin. Additional support for this contention arises from literature accounts claiming the accumulation of p-hydroxyphenyl units during the process of oxidative delignification with peroxyacids or laccase/mediator systems [13,14].

The data in Table II suggest that p-hydroxyphenyl units are oxidatively more stable than guaiacyl units, since the latter do not accumulate during oxygen delignification. Unfortunately, there are no literature accounts directly comparing the oxidative reactivity of p-hydroxyphenyl structures with their guaiacyl counterparts. To address this issue, we designed a set of experiments where two model compounds, namely 4-methylphenol and its guaiacyl counterpart, were oxidized under conditions resembling those of oxygen delignification. The products of the oxidation were then quantified by GC. It was found that 45% of 4-methylphenol remained unreacted, while only 12% of the guaiacyl phenol remained in the reaction mixture. In agreement with previous efforts [29], this experiment demonstrated the higher stability of p-hydroxyphenyl units under oxygen-delignification conditions. This provides additional evidence that their accumulation contributes to impairing the rate of the process as oxidation intensifies. Since considerably higher amounts of p-hydroxyphenyl

units exist in hardwood than in softwood, the accumulation of such units could be even more pronounced in oxygen delignification of hardwood pulps. This may, in part, explain the tendency of hardwood pulps to be more difficult than softwood pulps to delignify with oxygen [30].

CONCLUSIONS

The application of new spectroscopic methods has provided evidence for the presence of DPM structures in kraft and soda lignins. Independent dialyses and GC/MS analyses of fragmented (via the DFRC procedure) residual lignins isolated in high yields from the fibre, using novel procedures, has confirmed the presence of these structures in them.

The presence of dibenzodioxocins, responsible for the branching found in softwood lignin, has been confirmed and their abundance quantified. Dibenzodioxocin rings seem to be present in softwood lignin at a level of ~4% (per 100 C₉ units). Their reactivity under kraft pulping conditions causes the quantitative release of 5-5' biphenolic structures that seem to explain partly the ceiling encountered when alkaline pulps are subjected to oxygen delignification. Another factor responsible for the limits encountered during oxygen delignification seems to be the accumulation of relatively unreactive p-hydroxyphenyl structures within residual lignins.

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TABLE II
RELATIVE CONTENT OF
p-HYDROXYPHENYL UNITS
PRESENT IN THE PRODUCTS OF
ANALYTICAL PYROLYSIS OF
OXIDIZED RESIDUAL LIGNINS (%)

Time of Oxidation (min)	Relative Content of p-Hydroxyphenyl (%)
0	2.3
20	2.5
50	3.4
80	3.5
160	4.0

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