On the formation of diphenylmethane structures in lignin under kraft, EMCC®, and soda pulping conditions

Behzad C. Ahvazi, Gerry Pageau, and Dimitris S. Argyropoulos

Abstract: This paper describes our efforts focused at defining the formation of diphenylmethane moieties in lignin during conventional kraft and soda pulping conditions. This objective was realized by confirming, initially, the assignment of a ^{31}P NMR signal as being due exclusively to the presence of phosphitylated diphenylmethane (DPM) phenolic hydroxyl groups. More specifically, softwood milled wood lignin (*Picea mariana*) was subjected to kraft pulping conditions in the presence and absence of varying amounts of formaldehyde. After quantitative recovery of the lignin, the ^{31}P NMR spectra were recorded and the spectra revealed selective signal growth in the region confined between 142.8 and 144.3 ppm, in accordance with previous model compound work and detailed calculations based on the Hammett principles. To further substantiate our conclusions we also carried out two series of isothermal (120°C) kraft and soda pulping experiments followed by quantitative determinations of the DPM moieties, and correlated our findings with the differences in chemistry known to occur between the two processes. Finally, diphenylmethane phenolic moieties were determined in isolated residual lignins from two western hemlock kraft pulp samples produced via an EMCC® mill protocol and a laboratory batch digester, respectively. These structures prevailed amongst the condensed phenolic units of the conventional pulp, providing additional evidence to support the fact that modern modified pulping technologies beneficially alter the structure of residual kraft lignin.

Key words: phenyl groups, kraft pulping, modified kraft process, nuclear magnetic resonance (NMR), phosphorus spectroscopy.

Résumé : Dans ce travail, on décrit nos travaux orientés vers la démonstration de conditions de formation d'entités diphénylméthane dans les conditions de fabrication de pâtes kraft et à la soude. L'objectif de ces travaux a été réalisé en confirmant initialement l'attribution d'un signal RMN du ^{31}P uniquement à la présence de groupes hydroxyles phénoliques phosphylatés du diphénylméthane. D'une façon plus précise, on a soumis de la lignine de bois mou broyé (*Picea mariana*) à des conditions de fabrication de pâte kraft, en l'absence et en présence de quantités variables de formaldéhyde. Après avoir récupéré la lignine d'une façon quantitative, on a enregistré les spectres RMN du ^{31}P qui révèlent la croissance sélective de signaux dans la région comprise entre 142,8 et 144,3 ppm, en accord avec le travail antérieur sur un composé modèle et avec des calculs détaillés basés sur les principes de Hammett. Afin de confirmer nos conclusions, on a aussi effectué deux séries d'expériences isothermes (120°C) de formation de pâte kraft et de pâte à la soude, suivies de déterminations quantitatives des portions de DPM, et on a établi une corrélation entre nos résultats et les différences bien connues dans les chimies de ces deux procédés. Enfin, on a déterminé les portions phénoliques de diphénylméthane présentes dans des lignines résiduelles isolées à partir de deux échantillons de pâte kraft de la pruche de l'ouest obtenues respectivement par le biais d'un protocole EMCC® en usine et d'un lessiveur discontinu de laboratoire. Ces structures sont prévalentes dans les unités phénoliques condensées de la pâte conventionnelle; ces résultats fournissent des preuves supplémentaires relatives au fait que les technologies modernes de fabrication de pâte altèrent de façon avantageuse la structure de la lignine kraft résiduelle.

Mots clés : groupes phényles, fabrication de pâte kraft, procédé de fabrication kraft modifié, résonance magnétique nucléaire (RMN), spectroscopie du phosphore.

[Traduit par la rédaction]

Introduction

While the ether bonds of lignin cleave efficiently under alkaline pulping conditions, the formation of condensed structures decreases its reactivity and diminishes the solubility of the residual lignin (1). This phenomenon seriously interferes with the complete removal of lignin and the rate of delignification, especially during the final stages of most pulping processes.

During the past several years a number of modifications aimed at enhancing delignification have been proposed for the conventional kraft pulping process (2–5). Rapid displacement heating (RDH) (6–9) and modified continuous cooking (MCC) (10–13) are two examples of these processes. In addition, the

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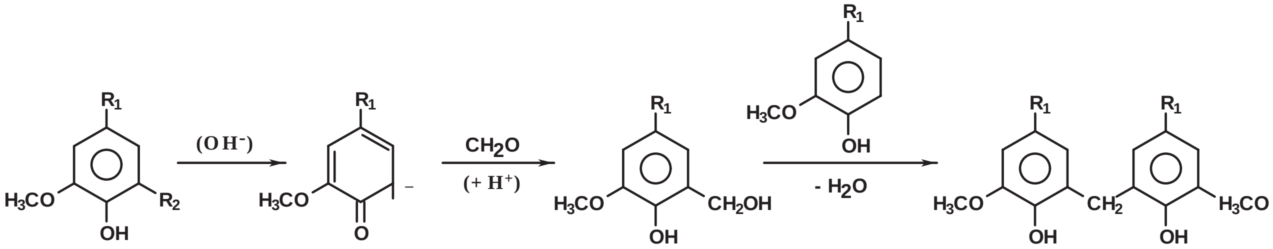
Scheme 1.

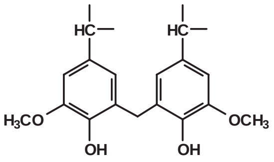


use of pulping additives such as polysulphide (14–16) and anthraquinone (16–18) have also been advocated.

Amongst the reactions that are known to interfere with the process of alkaline delignification are those involving the formation of carbon–carbon bonds. Formaldehyde is known to be liberated (19) as early as 100°C, as a result of C_γ elimination from phenylcoumaran (20, 21) and from guaiacylglycerol-β-aryl ether structures, both abundant in native lignin (22–24). The released formaldehyde is known to cause the substitution of hydroxymethyl groups at positions *ortho* to the phenolate moieties (22). This potentially represents a very important reaction since one third of the phenolic nuclei in softwood kraft lignin (25) and about one half of the phenolic and non-phenolic units in softwood milled wood lignin contain free C5 positions (23). The methylolated phenols may undergo further reaction to yield diphenylmethane moieties (1, 26, 27) (Scheme 1).

A number of these structures (**1**–**4**) have been suggested (28–31). Another condensation reaction caused by the liberation of formaldehyde during alkaline hydrolysis is Tollen's reaction (1). This reaction involves the substitution of hydroxymethyl groups at side-chain positions provided activating carbonyl groups are present (1, 25).

Although several studies by Chiang and Funaoka (32–34) have claimed to show convincing qualitative and quantitative evidence for the presence of diphenylmethanes in residual kraft lignin, a number of questions in relation to the method of detection have recently surfaced (35). Since the development of ^{31}P NMR spectroscopy for probing lignin structure (36–40), the technique has been successfully implemented for the absolute determination of the various phenolic and non-phenolic structures in several native and technical lignins (41–44). The availability of a phosphitylating reagent (40) that permits excellent resolution and the quantitative spectroscopic detection of several phenolic moieties with varying substitution patterns (44–46) provides an excellent opportunity for systematically exploring the complex reactions that occur in lignin during alkaline pulping. For example, such an effort has already led to the definition of the fundamental thermodynamic parameters that govern the stereoselective degradation of the arylglycerol-β-aryl ether bonds in milled wood lignin under kraft pulping conditions (47).



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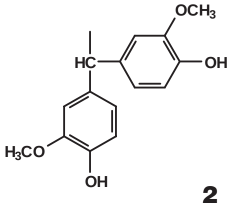

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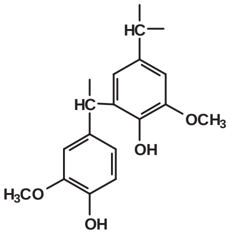

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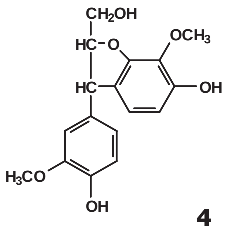

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As mills move toward elemental chlorine free bleaching (ECF), the negative impact of condensed lignin structures on the final pulp brightness ceiling provides additional incentives to minimize the possibility that condensation reactions may occur in the digester and during oxygen delignification. The precise identification of such structures and their formation kinetics could be a major step forward toward understanding and minimizing their detrimental effects.

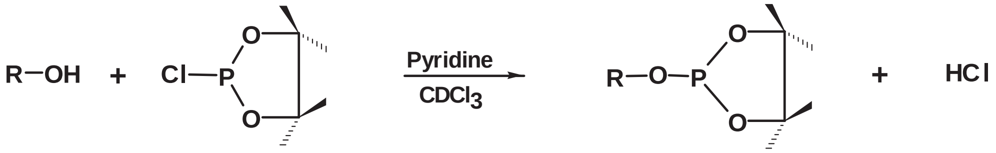
In this paper we describe our efforts focused on defining the formation of diphenylmethane moieties in lignin during conventional kraft and soda pulping conditions. This objective was realized by initially confirming the assignment of a ^{31}P NMR signal as being due exclusively to the presence of phosphitylated diphenylmethane phenolic hydroxyl groups. The overall phosphitylation reaction of labile protons is depicted in Scheme 2. We then accumulated kinetic data for the formation of these species under soda and kraft pulping conditions and correlated this information to known chemistry.

Experimental

Treatment of milled wood lignin under homogeneous kraft or soda pulping conditions

Initially, a white liquor solution containing 7.0 g of sodium hydroxide (0.175 mol NaOH) and 6.2 g of sodium sulphide (0.026 mol $Na_2S{\cdot}9H_2O$) per 100 mL deionized water was prepared. For the case of the soda "cooks" the molar amount of sodium sulphide ($Na_2S{\cdot}9H_2O$) used for the kraft pulping experiments was substituted with sodium hydroxide dissolved in 200 mL of deionized water and dioxane (1:1 v/v). This solution was then mixed with an equal volume of dioxane. During a typical experiment, 0.1 g of softwood milled wood lignin, prepared according to the Björkman procedure (47, 48) and having the following elemental composition: 60.86% carbon, 5.71% hydrogen, and 15.45% methoxy, was used. This lignin was dissolved in 1.33 g of the previously described white

Scheme 2.



liquor (the ratio of liquor to lignin was 4:1). The reaction was carried out in a 10 mL stainless steel bomb whose air was displaced by nitrogen. The kraft cooking was simulated by heating and occasionally shaking the bomb in an oil bath preheated to the desired temperature and for specific time intervals. At the end of the reaction period, the bomb was cooled with cold water and its contents were acidified to pH 2 using dilute hydrochloric acid (0.2 M HCl). The precipitate was allowed to settle overnight. It was then collected by centrifugation and washed with acidic water to remove the inorganic salts. The precipitated degraded lignin was then freeze-dried and brought to constant weight at room temperature under reduced pressure. This material accounted for approximately 80% of the initial weight of lignin used. In an effort to isolate the remaining 20%, the solution containing the water-soluble low molecular weight lignin resulting from the first aqueous acidic precipitation was allowed to dry at room temperature. The remaining low molecular weight lignin was extracted by addition of 10–15 mL high-grade tetrahydrofuran. This was followed by evaporation of the solvent to a fine viscous residue, and dropwise addition to 20 mL of diethyl ether. This step was repeated 2–3 times, allowing the collection of more lignin, free from inorganic salts. Finally, the diethyl ether was evaporated and the remaining lignin was freeze-dried. The samples, after being brought to constant weight under reduced pressure, accounted for almost 16% of the starting lignin. The two sets of degraded lignin samples collected were then mixed thoroughly prior to subsequent analyses.

Addition of formaldehyde to milled wood lignin followed by homogeneous kraft pulping

Milled wood lignin (100 mg) was placed in a 10 mL stainless steel bomb. The lignin was then dissolved by the addition of 1.33 g of white liquor solution, prepared by dissolving 7.0 g of sodium hydroxide (NaOH) and 6.2 g of sodium sulphide ($Na_2S \cdot 9H_2O$) in a solution (200 mL) of deionized water and absolute dioxane (1:1 v/v). Two separate sets of experiments, in which the amount of formaldehyde added was varied, were carried out at 120°C. For the first series of experiments, 11.1 μL of a 30% formaldehyde solution, accounting for 50% of the total β-aryl ether bonds, was added to each sample, while for the second series, 22.2 μL (representing 100% of the total β-aryl ether bonds) was added. After replacing the air with nitrogen, each bomb was sealed. Four reaction bombs (each containing the above mixture) were then placed in a preheated oil bath and after occasional shaking they were removed after 1, 2, 3, and 4 h of treatment. The isolation and purification procedures were conducted in a manner identical to those discussed in the previous section.

Preparation of kraft pulps and residual lignin isolation

A conventional western hemlock kraft pulp was prepared at Paprican in a laboratory batch digester using conditions described previously (46). The western hemlock EMCC® (extended modified continuous cooking) pulp was supplied by a Canadian mill. The isolation of residual lignin was carried out from pre-extracted pulp meal following a procedure described previously (46).

Quantitative ^{31}P NMR spectroscopy

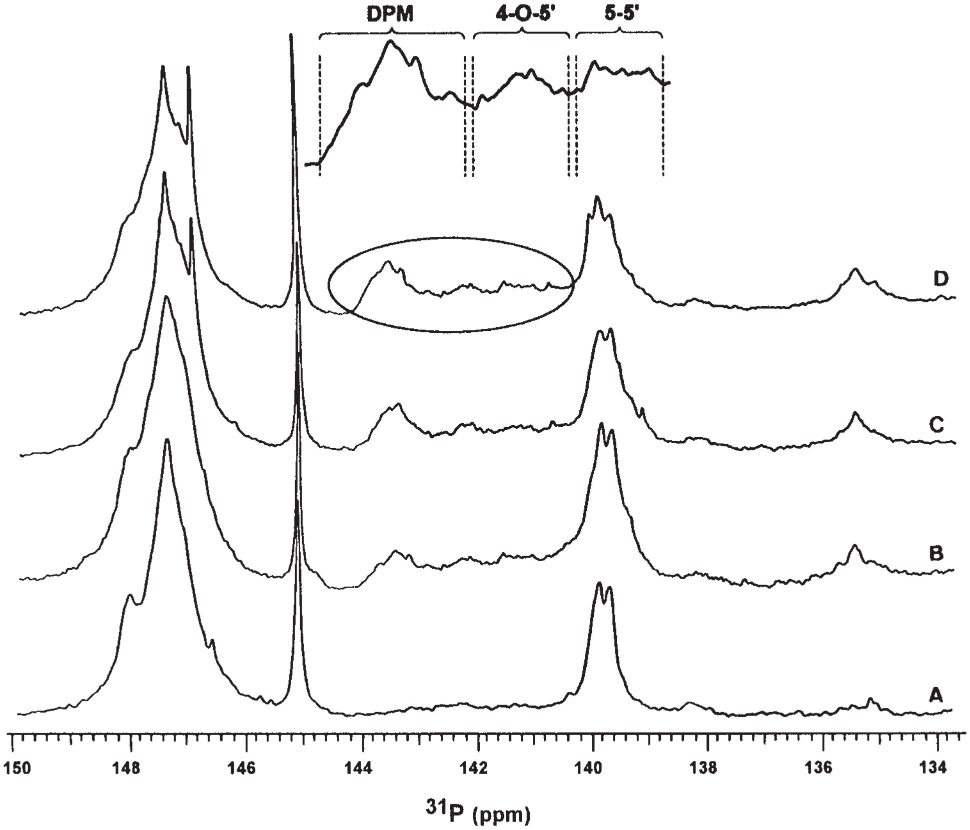
The derivatizing reagent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was synthesized (40) and used as the phosphitylation reagent. Approximately 30 mg of dry lignin was added to 800 μL of a solvent mixture containing pyridine and $CDCl_3$ at a volume ratio of 1.6:1. The mixture was stirred with a magnetic bar until the lignin was fully dissolved. This was followed by the addition of 100 μL of a solution containing both cyclohexanol (11 mg/mL) as an internal standard and chromium acetylacetonate (5 mg/mL) as a relaxation reagent. Finally, 100 μL of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was added and the flask was sealed and shaken to ensure thorough mixing. The ^{31}P NMR spectra were obtained by using inverse gated decoupling on a Varian XL-300 FT-NMR spectrometer at 121.5 MHz. The obtained spectra were integrated 3 times on separate occasions and the resulting data were averaged out as reported here. Further details dealing with acquisition and spectral processing have been described elsewhere (40, 49).

Results and discussion

In our earlier work the phosphorus NMR spectra of solubilized kraft lignin contained, among others, a signal centred around 143.5 ppm (40). On the basis of model compound work and calculations based on the Hammett principles (50), this signal was tentatively assigned to diarylmethane structures possessing free phenolic hydroxyl groups (40). In an effort to confirm the validity of our earlier work, the interaction of milled wood lignin with formaldehyde under kraft pulping conditions was clarified by conducting experiments in which different amounts of formaldehyde were introduced into the reaction mixture prior to the cook. More specifically, two different sets of experiments were carried out with four samples of milled wood lignins being subjected to kraft pulping at 120°C with the addition of formaldehyde accounting for 50 and 100% of the total aryl ether units of lignin, respectively (51). After quantitative recovery of the lignin, the ^{31}P NMR spectra were recorded and the spectra critically examined. Figure 1 shows a representative series of such spectra.

A comparison of the ^{31}P NMR spectra of milled wood lignin (*A*) to those treated under kraft pulping conditions without (*B*) and with (*C* and *D*) addition of formaldehyde reveals substantial signal growth (Table 1) at around 143.5 ppm. Indeed, the area under the broad signal (142.8–144.3 ppm), labelled DPM, was increased in spectra *C* and *D* where significant amounts of formaldehyde had been added (Table 1). In addition, the spectra of the samples to which formaldehyde was

Fig. 1. Quantitative ^{31}P NMR spectra of milled wood lignin before and after being subjected to isothermal (120°C, 3 h) homogeneous kraft pulping conditions; (*A*) blank, (*B*) control kraft pulping, (*C*) with the addition of 11 μL, and (*D*) 22 μL formaldehyde corresponding to 50% and 100% of the aryl ether structures in lignin.



added display a new signal at 147.01 ppm that appears in the aliphatic OH region. In accordance with the chemistry of the formaldehyde–phenol interaction, which is known to occur under alkaline conditions (19, 20), it is very likely that this signal is due to the aliphatic primary hydroxyl group of methylolated aromatic rings.

When the ^{31}P NMR signal in the region 142.8–144.3 ppm was integrated, the determination of the actual concentrations of diphenylmethane structures in milled wood lignin, in the presence and absence of formaldehyde under kraft pulping conditions, was made possible as a function of reaction time at 120°C (Table 1).

The quantitative data thus collected revealed that under isothermal conditions (120°C) the addition of formaldehyde to the kraft reaction medium causes the buildup of DPM structures within lignin, while in the absence of externally added formaldehyde, these structures predominate after 3–4 h of reaction. It is also interesting to note that when a large excess of formaldehyde was added (amounting to 100% of the total aryl ethers) the amount of DPM structures reached a value of 0.4 mmol/g within 60 min at 120°C, remaining approximately constant beyond this point.

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 moieties, and correlated our findings with the differences in chemistry known to occur between the two processes.

Table 1. Showing the actual amounts of DPM[a] structures present in MWL[b] before and after the addition of formaldehyde[c] under homogeneous kraft pulping conditions.[d]

	DPM × 10^4 (mol/g)		
Reaction time (min)	Control kraft	50%[c]	100%[c]
60	0.83	1.60	4.0
120	1.41	2.20	4.2
180	2.41	3.00	4.4
240	4.10	4.10	4.6

[a] Diphenylmethane structures.

[b] Milled wood lignin (softwood, *Picea mariana*).

[c] Amount of formaldehyde added, expressed as percentage of the total amount of aryl ethers present in MWL.

[d] The temperature of the kraft pulping experiment was set at 120°C.

The data of Table 2 clearly demonstrate that the formation of diphenylmethane moieties 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, 52, 53).

The presence of sulphide ions within sulfate liquors has been suggested to preclude the liberation of formaldehyde from the lignin biopolymer (19). Alternatively, the absence of sulphide, i.e., soda pulping, allows the intermediate quinone-

Scheme 3.

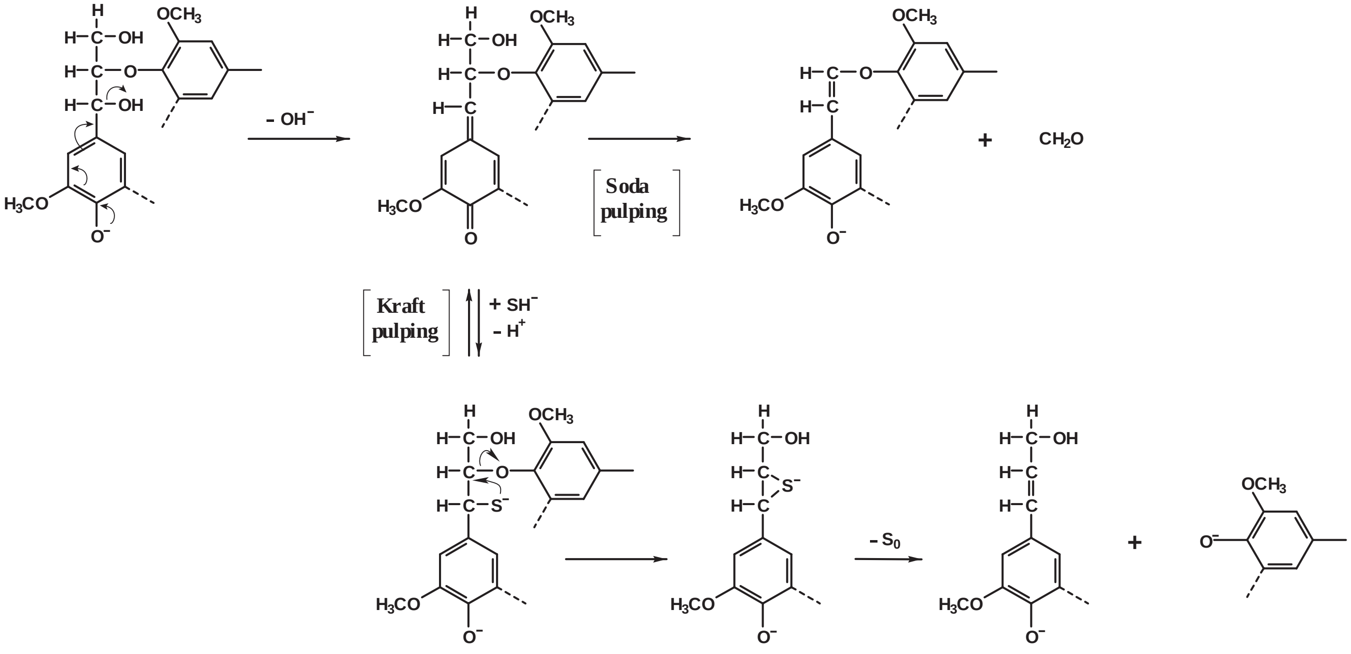


Table 2. Showing the actual amounts of DPM[a] structures present in MWL[b] under homogeneous kraft and soda[c] pulping conditions.[d]

	DPM × 10^4 (mol/g)	
Reaction time (min)	Kraft pulping	Soda pulping
60	0.83	1.60
120	1.41	2.20
180	2.41	3.10
240	4.10	4.30

[a] Diphenylmethane structures.
[b] Milled wood lignin (softwood, *Picea mariana*).
[c] Amount of sodium sulphide was replaced with sodium hydroxide.
[d] The temperature of the pulping experiments was set at 120°C.

Table 3. Showing the actual distribution of condensed and diphenylmethane structures present in conventional and EMCC® kraft pulps of similar κ number.

	Total concentration × 10^4(mol/g)	
Pulp sample identity	Condensed units[a]	DPM units[b]
Conventional kraft (κ = 26.8)[c]	17.0	3.0
EMCC® kraft (κ = 26.0)[c]	15.0	2.0

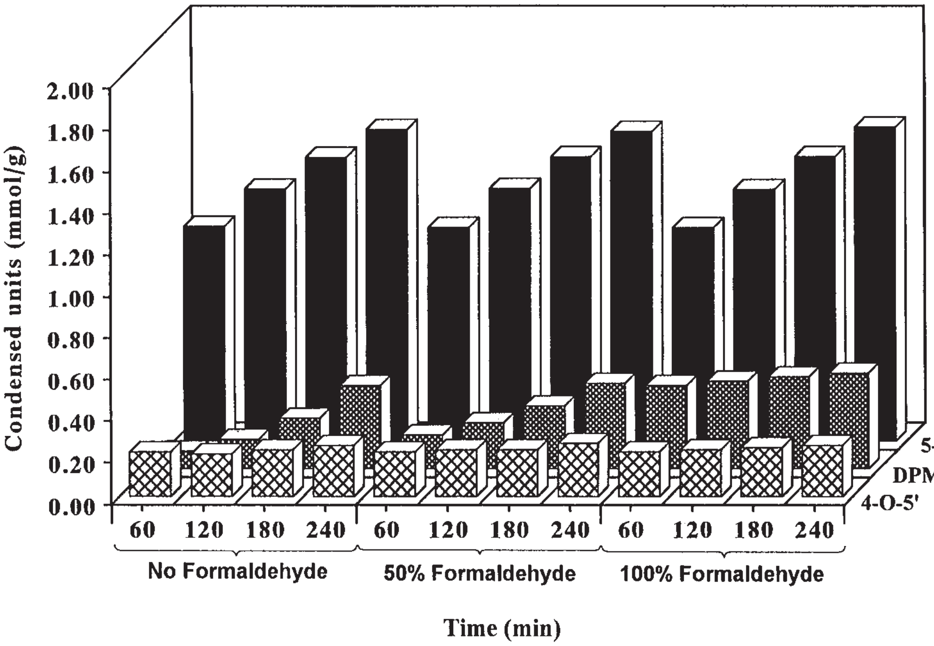
[a] Total condensed phenolic structures.
[b] Diphenylmethane phenolic OH structures.
[c] κ number.

methides to lose formaldehyde, causing the formation of undesirable alkaline stable enol ethers (1, 54). The rate data of Table 2 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 κ (kappa) number (55) (Scheme 3).

Among the various principles that operate during modified pulping, the control of alkalinity is of prime importance. Maintaining hydroxide concentration at a uniformly low level offers distinct advantages as far as carbohydrate degradation is concerned. In this context, maintaining a uniformly low alkalinity may also have an impact on the actual amount of diphenylmethane structures that form within the residual kraft lignin. For this reason residual lignin was isolated from two hemlock kraft pulp samples (κ number 26.0) produced via an EMCC® mill protocol and a laboratory batch digester, respectively. The data of Table 3 are in accord with the previous observations. While in the conventional kraft pulp the overall amount of C-5 substituted phenolic environments is higher by 11%, the diarylmethane structures prevail amongst them by 37%. These data, coupled with the earlier account of Froass et al. (43), provide convincing evidence supporting the fact that modern modified cooking technologies alter the structure of lignin beneficially.

The region of the ^{31}P NMR spectra assigned to the overall condensed phenolic units (140.2–144.3 ppm), in addition to the diphenylmethane moieties, also includes phenolic hydroxyl groups belonging to 4-O-5′ and 5,5′ structures. More specifically, on the basis of model compound work and detailed calculations these structures have been assigned to the signals ranging between 142.8 and 141.7 ppm and 141.7 and 140.2 ppm, respectively (40, 50) (Fig. 1). This assignment was also confirmed by the efforts of Smit et al. (44). In 1995, Brunow's group announced the discovery of the dienzodioxocin bonding patterns as being prevalent in softwoods lignins (56, 57). This involves the formation of α,β ethers on the same 5–5′ biphenyl structure. The new moiety, when subjected to soda pulping conditions, was shown to release significant amounts of structures bearing 5,5′ biphenolic hydroxyl groups (58). Therefore under kraft pulping conditions it is likely that similar reactions, releasing 5,5′ biphenolic hydroxyl groups,

Fig. 2. Kinetic data showing the development of the actual amounts of 4-*O*-5′,5,5′ biphenolic and diphenylmethane phenolic hydroxyl structures on softwood milled wood lignin under homogeneous kraft pulping conditions at 120°C in the presence and absence of formaldehyde. The amount of formaldehyde added is expressed as percentage of the total amount of aryl ethers present in MWL.



will occur. The data of Fig. 2 show that indeed such structures are released in very significant amounts after 4 h at 120°C (about 1.5 mmol/g are formed within milled wood lignin). As anticipated, the presence of formaldehyde does not seem to affect the rate of formation of 5,5′ biphenolic hydroxyl groups or the concentration of dibenzyl ether (4-O-5′) structures (Fig. 2).

Finally, the formation of diphenylmethane structures under kraft and soda pulping conditions was found to follow pseudo-first-order kinetics with rate constants $14.8 \times 10^{-5} \pm 2.2 \times 10^{-7}$ s^{-1} and $9.2 \times 10^{-5} \pm 8.8 \times 10^{-7}$ s^{-1}, respectively.

Conclusions

By using quantitative ^{31}P NMR spectroscopy it is possible to identify, quantify, and follow the formation of phenolic hydroxyl groups that belong to diphenylmethane units under kraft and soda pulping conditions. These units exhibit a ^{31}P chemical shift signal that is confined between 142.8 and 144.3 ppm. Data derived during the course of this work implied that diphenylmethanes are formed in higher quantities during a conventional pulping than are their EMCC® counterparts, at the same κ number.

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