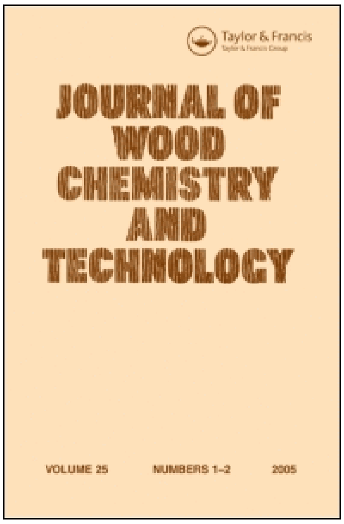
This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

The Condensation Reactions of Lignin Model Compounds in Alkaline Pulping Liquors

Terry J. Fullerton[a]
[a] Pulp and Paper Research Organisation of New Zealand, Forest Research Institute, Rotorua, New Zealand

To cite this Article Fullerton, Terry J.(1987) 'The Condensation Reactions of Lignin Model Compounds in Alkaline Pulping Liquors', Journal of Wood Chemistry and Technology, 7: 4, 441 — 462
To link to this Article: DOI: 10.1080/02773818708085279
URL: http://dx.doi.org/10.1080/02773818708085279

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 7(4), 441-462 (1987)

THE CONDENSATION REACTIONS OF LIGNIN MODEL COMPOUNDS IN ALKALINE PULPING LIQUORS

Terry J. Fullerton
Pulp and Paper Research Organisation of New Zealand,
Forest Research Institute, Private Bag,
Rotorua, New Zealand

ABSTRACT

The significance of condensation reactions at the 5-position of the aromatic ring of lignin to the overall pulping process has been evaluated using lignin model compounds. Reactions of 5-hydroxymethylcreosol, as a model for 5-substituted lignins formed when formaldehyde is released during pulping, have shown that such groups will react via ortho-quinonemethides to give alkali-stable carbon-carbon bonded condensation products. The amount of condensation depends on the type of pulping liquor used, with less formed in the kraft and soda-anthraquinone (AQ) processes than in the soda process. In these liquors the hydrosulphide or anthrahydroquinone (AHQ) ions present can compete effectively with phenoxide ion for the reactive o-quinonemethide intermediate.

Reduced AQ reacts with the o-quinonemethide to form oxanthrone- and anthrone-adducts which are still detectable at 170°C. Such reactions, particularly the reduction of AQ to its anthrone oxidation state, may be one of the reasons why AQ is consumed during pulping. Degradation products of glucose have also been found to decrease the amount of lignin-lignin type condensation products.

INTRODUCTION

In the study of the chemistry of pulping processes most of the attention has focussed on the reactions leading to fragmentation of the lignin. By comparison the condensation reactions[1] which occur during pulping have received far less attention and yet, as pointed out by Hägglund[2] as early as 1941, the amount of condensation occurring may significantly affect the delignification rate. The emphasis on the fragmentation of lignin is clearly illustrated in the publications relating to the chemistry of anthraquinone (AQ) pulping. Numerous papers have been published describing the cleavage of β-ether bonds by AQ[3,4] but few have discussed the influence of AQ on the extent of the condensation reactions[5].

The most common types of lignin condensation reactions are believed to be those which occur when formaldehyde, liberated from the γ-carbon of the phenylpropane side chain, reacts with the free 5-position of a phenolic lignin unit leading to formation of a 5-hydroxymethyl lignin. This may then react further to generate alkali-stable diphenylmethane bridges in the lignin. It is likely that the condensation of the lignin in this way will be dependent on the nature of the pulping liquors and that processes which minimize this sort of reaction are likely to be more efficient. This is supported by recent studies using C-14 labelled wood[6] and oxidative degradation of the lignin in the pulp[7] which have shown that in the very efficient kraft process such condensation reactions are minimized.

Different types of pulping liquors will also affect the amount of formaldehyde released from the lignin. As is well known from lignin model compound studies, phenolic β-ether units react under soda conditions to form enol ethers with loss of formaldehyde whereas under kraft or soda-AQ conditions the β-ether bonds are cleaved to generate new free phenolic units[8]. Decreased formaldehyde production may in itself be one reason for the more rapid rate of pulping in the kraft and soda-AQ processes.

Even in the kraft and soda-AQ processes, however, formaldehyde will be released from some of the units in the lignin polymer. In particular, carbon-carbon bonded β-5 phenyl coumarans and β-1 type structures will both lose formaldehyde to form the corresponding stilbene structures. The preference for this reaction over any nucleophilic addition to the intermediate quinonemethide is illustrated by the failure of strong nucleophiles such as anthranol and AHQ anions to form adducts with these compounds[9].

It was therefore the objective of the present study to develop an improved pulping process by minimizing the lignin condensation reactions which can occur. For this reason the reactions of a 5-hydroxymethyl substituted lignin model compound in various pulping liquors have been investigated.

RESULTS AND DISCUSSION

Selection of a Lignin Model Compound

The lignin model compound selected for the initial part of this study was the 5-hydroxymethyl substituted creosol, 1. A creosol was chosen because it is the simplest example of a compound bearing the same aromatic substitution pattern as softwood lignin. A methyl group was preferred to a substituted propyl substituent because it was expected to give a simpler product mixture and yet is not likely to effect the reactivity of the 5-hydroxymethyl group.

Reaction in Sodium Hydroxide Solution

Reaction of the model compound 1 in 1N NaOH in a sealed glass tube at 135°C for 1 hour gave the dimer 2, plus unreacted starting material and a small amount of p-creosol arising from the reversal of formaldehyde addition.

The reaction can be explained as shown in Figure 1 where compound 1 is converted to an ortho-quinonemethide which can

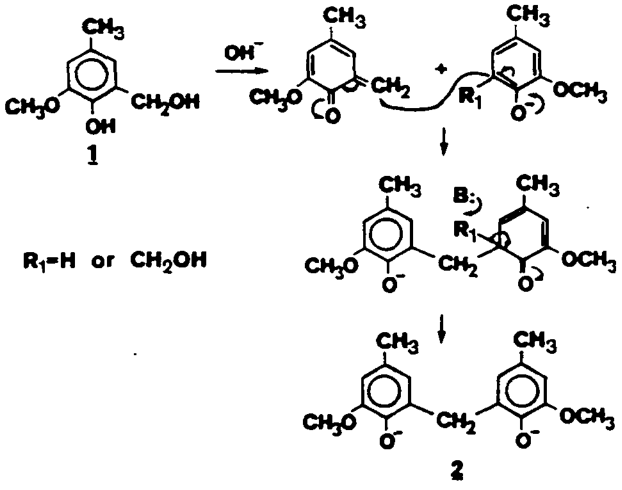


FIGURE 1 Mechanism of formation of diphenylmethane 2.

then react either with p-creosol (R_1 = H) or with starting material 1 (in this case the intermediate would lose formaldehyde). Both routes would lead to the same diphenylmethane 2. This dimer is also obtained when creosol and formalin are heated together in 2N NaOH at 165°C[10].

The rate of formation of dimer 2 and the rate of the reaction of the starting material 1 in 1N NaOH are shown in Figure 2. The product mixtures were analysed by reverse phase HPLC of the dichloromethane extracts of the cooled acidified solutions using p-cresol as the internal standard.

Reaction in Kraft White Liquor

When 5-hydroxymethylcreosol 1 was reacted under the same conditions in kraft white liquor, only minor amounts of the dimer were obtained. The major product in this case was

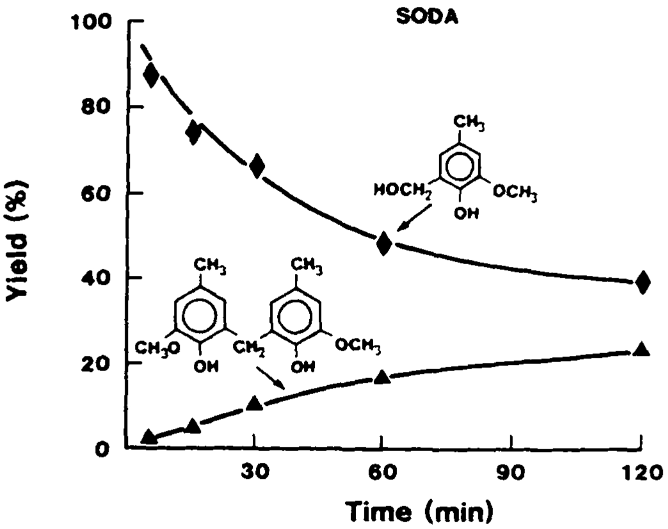
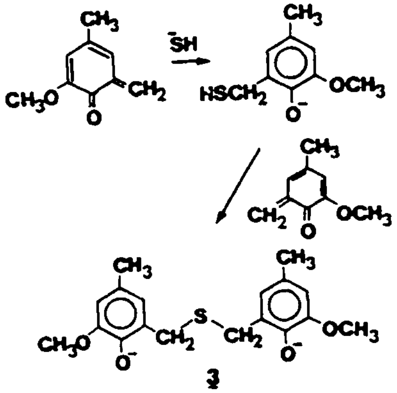


FIGURE 2 Reaction of 5-hydroxymethylcreosol in 1N NaOH at 135°C (Yield as % of theoretical moles of product).

identified as the sulphur dimer 3 together with smaller amounts of thiol 4 and disulphide 5.

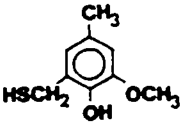
The formation of these products is consistent with the reaction pathway shown in Figure 3 in which the hydrosulphide ion attacks the intermediate *o*-quinonemethide to form the methylene thiol 4. This may then react with a second *o*-quinonemethide to give the observed monosulphide dimer 3 as the major product or alternatively this product and the disulphide 5 may both be formed during work-up by air oxidation of the thiol.

The rates of consumption of starting material and of formation of dimers in the kraft liquor are shown in Figure 4. By comparison with Figure 2 it is apparent that hydrosulphide ion leads to a considerably faster consumption of starting material than hydroxide alone, and competes very efficiently

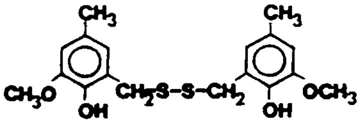


3

FIGURE 3 Mechanism of formation of kraft products.



4



5

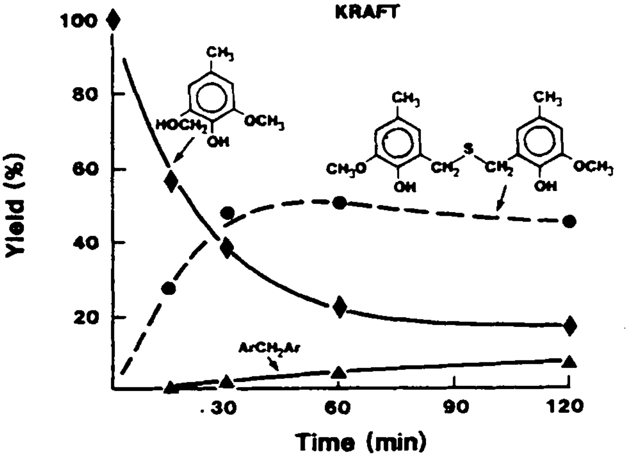


FIGURE 4 Reaction of 5-hydroxymethylcreosol in kraft liquor at 135°C.

with phenoxide ion for the intermediate o-quinonemethide, leading predominantly to formation of the sulphur-bridged dimer 3 in preference to the non-sulphur dimer 2.

These results are in complete agreement with Hästbacka's early results with vanillyl alcohol[11,12] in which white liquor was found to inhibit dimerisation and give a high yield of vanillyl monosulphide and also Smith and Dimmel's more recent results in which a sulphur dimer of syringyl alcohol was reported[13]. These results have been taken to be evidence of condensations occurring at the α-carbon of the lignin polymer; however, as there are not believed to be any C-1 primary alcohol structures in lignin, it is necessary to assume that secondary alcohols will react in a similar manner. No such assumption is necessary when considering the reactions of primary alcohols at C-5 as these groups will be generated whenever formaldehyde reacts with lignin at the C-5 position.

A comparison of the reactivities of vanillyl alcohol and 5-hydroxymethylcreosol shows that vanillyl alcohol reacts more rapidly than 5-hydroxymethylcreosol. As shown in Table 1 for the reaction of the two compounds at 100°C in sodium hydroxide and kraft white liquor, the recovery of unreacted 1 was greater than the recovery of vanillyl alcohol in both cases.

Reaction in Soda-AQ Liquors

One of the major objectives of this study was to determine if the active components of soda-AQ liquors might also interfere with the formation of condensation products and so contribute to the faster removal of lignin in the soda-AQ process. To investigate this, 5-hydroxymethylcreosol 1 was heated in 1N NaOH with 1 equivalent of AQ and 5 equivalents of glucose (to act as a reducing source for AQ).

TABLE 1: Reaction of Model Compounds at 100°C

Compound	Liquor	Time (min)	% unreacted starting material
5-$HOCH_2$-creosol	1N NaOH	30	98.3
5-$HOCH_2$-creosol	1N NaOH	120	87.8
5-$HOCH_2$-creosol	Kraft white liquor	30	93.0
5-$HOCH_2$-creosol	Kraft white liquor	120	80.5
Vanillyl alcohol	1N NaOH	120	67.6
Vanillyl alcohol	Kraft white liquor	120	24.6

As shown in Figures 5 and 6, the addition of AQ does result in a more rapid consumption of starting material and less of the diphenylmethane dimer 2 being formed, although, as discussed below, interpretation of the results is complicated by the fact that glucose alone produces a similar effect. In order to overcome this difficulty, the reaction was repeated without glucose but using instead 1 equivalent of oxanthrone (as the reduced form of AQ). Once again, less dimer was formed compared to the soda control, indicating that the AHQ competes effectively with phenoxide ion for the intermediate o-quinonemethide.

AQ Adducts

Both the soda-AQ-glucose and soda-oxanthrone reaction products contained AQ-adducts. When 0.1 equivalents of reduced AQ or oxanthrone were used, the substituted oxanthrone 6 was obtained as the major product whereas with 1 equivalent of oxanthrone, the substituted anthrone 7 was the preferred product. The formation of these adducts is analogous to the formation of oxanthrone and anthrone adducts from the reaction of vanillyl alcohol with AHQ[14,15].

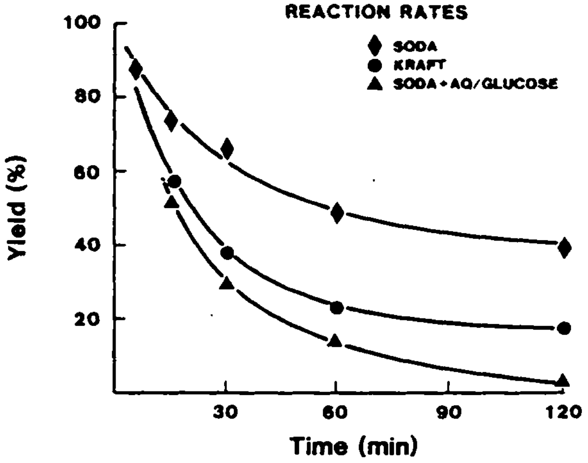


FIGURE 5 Relative reactivity of 5-hydroxymethylcreosol in soda, kraft and soda + AQ/glucose solutions at 135°C.

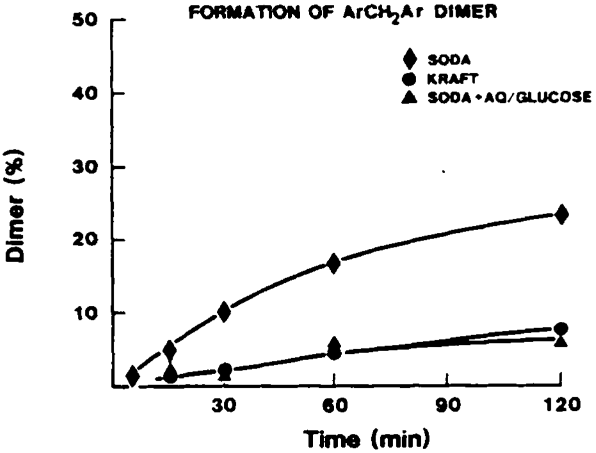
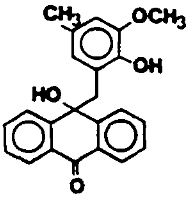
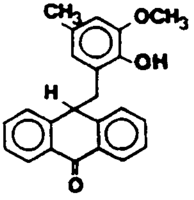


FIGURE 6 Rates of formation of diphenylmethane in soda, kraft and soda + AQ/glucose solutions at 135°C.



6



7

The ratio of the two compounds 6 and 7 obtained under different conditions was determined by HPLC and is summarised in Table 2. The two compounds were readily separated from each other and from other compounds of the mixture by using the HPLC conditions used for analysis of the soda and kraft products. The yields given for the anthrone adduct should be considered minimum values as this type of compound readily undergoes air oxidation to the corresponding oxanthrone adduct. In the absence of air the compounds are remarkably stable and are even detected in the products from the 170°C cook.

Both adducts gave distinctive pmr spectra from which the ratio of the two components in the reaction mixture could also be determined on the basis of the ratio of the two methoxyl peaks at δ 3.68 and δ 3.81 for the oxanthrone and anthrone adducts respectively. It is interesting to note that these methoxyls are not shifted upfield as much as the corresponding vanillyl adducts[15] which occur at δ 3.30 and δ 3.42 even though the methoxyl substituent is in the same position relative to the AQ ring system in both cases. This suggests that in the *o*-quinonemethide adducts the phenolic ring is not located as directly in the shielding zone over the AQ ring system as in the vanillyl adducts[14].

The formation of anthrone adducts like 7 is of particular interest because it results in AQ being 'deactivated' and no

TABLE 2: HPLC Analysis of AQ Adducts

Reactants	Temp (°C)	Time (min)	Oxanthrone Adduct 6 % yield	Anthrone Adduct 7 % yield	Ratio 6/7
0.1 AQ/glucose	135	15	0.9	0.07	12.6
		30	2.5	0.15	16.8
		60	1.9	0.2	9.4
		120	6.8	0.7	10.5
0.1 oxanthrone	135	120	0.7	0.09	7.8
1.0 oxanthrone	135	120	6.6	10.9	0.6
1.0 oxanthrone	170	120	1.3	2.3	0.6

longer available to take part in the AQ-AHQ catalytic cycle. Loss of AQ by the further reduction of AHQ or an oxanthrone adduct to anthranol intermediate was also found to be involved in the formation of 3-guaiacylbenzanthrone during AQ pulping[16]. How these reductions occur remains unknown with both radical[15] and ionic mechanisms being possible.

The decreased amount of dimer 2 formed when reduced AQ is present and the isolation of adducts 6 and 7 again confirm the intermediacy of an o-quinonemethide in the reaction mixture and suggest that, as with the kraft process, competition for the o-quinonemethide by the nucleophilic AHQ dianion may limit the condensation reactions leading to diphenylmethane structures during pulping.

Reactions With Glucose

In considering the reactions that an o-quinonemethide of lignin is likely to undergo under pulping conditions it is important to include those reactions which may occur between this reactive intermediate and carbohydrate degradation products released during pulping. An example of the possible role played by enediols derived from carbohydrates in pulping is illustrated by previous work with ß-ether lignin model compounds in which it was shown that such compounds could be cleaved efficiently with reducing sugars[17]. The participation of an enediol in this reaction was indicated by the isolation and subsequent fragmentation of a carbon-carbon bonded ß-ether - ascorbic acid intermediate[18].

In the present study, the role of carbohydrate degradation products was investigated by repeating the soda and white liquor reactions in the presence of 5 equivalents of glucose. The results are shown in Figures 7 and 8. In both cases the amount of $ArCH_2Ar$ dimer formed is very small, indicating that the carbohydrate degradation products will compete efficiently for the intermediate o-quinonemethide. In the kraft case some sulphur dimer 3 is still formed, although to a lesser extent than when glucose is absent. Whereas in the previous HPLC analyses complete separation of all components was obtained, for the reactions with glucose present a continuum of products absorbing at 282 nm that eluted with the dimers was obtained. Reaction of 5-hydroxymethylcreosol 1 with 5 equivalents of bleached pulp in 1N NaOH gave similar yields of dimer and starting material to the soda control confirming that it is carbohydrate degradation products rather than the carbohydrate itself which is reacting with the o-quinonemethide.

Reactions at 170°C

A temperature of 135°C was chosen for most of the work in this study as it was considered that use of this temperature would be high enough for o-quinonemethide formation to occur and yet not so high that the intermediate compounds formed would be unstable. A limited number of reactions was also done at 170°C

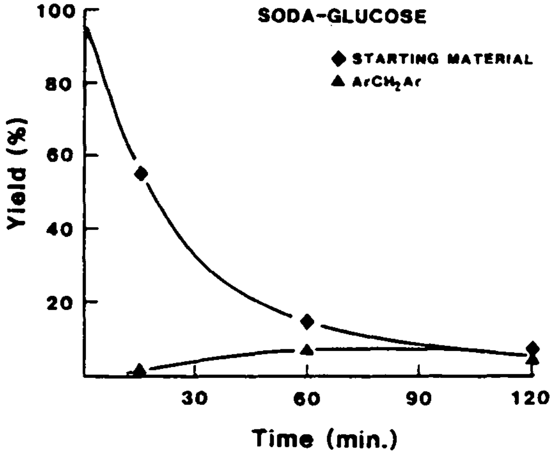


FIGURE 7 Reaction of 5-hydroxymethylcreosol with glucose in 1N NaOH at 135°C.

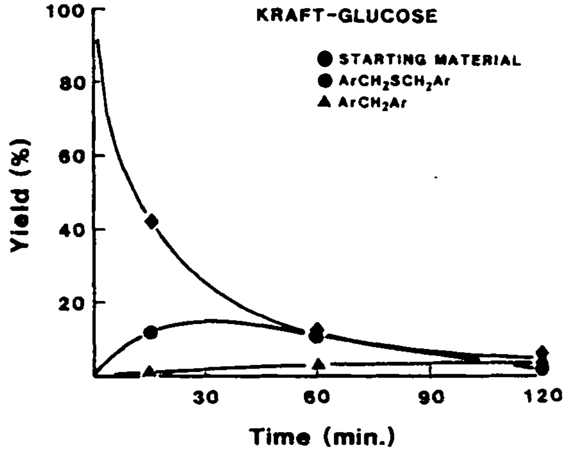


FIGURE 8 Reaction of 5-hydroxymethylcreosol with glucose in kraft liquor at 135°C.

TABLE 3: Reaction of Model Compounds at 170°C

Compound	Liquor	% 5-$HOCH_2$-creosol	% $ArCH_2Ar$* $\underline{2}$	% Creosol
5-$HOCH_2$-creosol	1N NaOH	1.6	44.8	14.5
5-$HOCH_2$-creosol	Kraft white liq.	3.4	29.5	14.6
$ArCH_2SCH_2Ar$	1N NaOH	11.9	11.4	25.6
$ArCH_2SCH_2Ar$	Kraft white liq.	6.2	0.0	19.9

* Ar = 5-substituted creosol.
Yields are given as % of the theoretical moles of product.

to simulate pulping conditions. These reactions were done in Teflon-lined stainless steel reactors. The results obtained are summarised in Table 3.

The sulphur dimer 3 was not found in any of the products indicating that it is not stable under pulping conditions. However, the lower yield of the diphenylmethane 2 in the presence of white liquor suggests that the hydrosulphide ion is still interfering in some way with the formation of the diphenylmethane condensation product.

CONCLUSIONS

The much smaller amounts of the diphenylmethane condensation product 2, formed by the reaction of 5-hydroxymethylcreosol in kraft and soda-AQ liquors than in soda liquors, is consistent with previous findings that the lignin in kraft lignin is not highly condensed[6,7]. However, the predominance of this condensation under soda pulping conditions and the isolation of

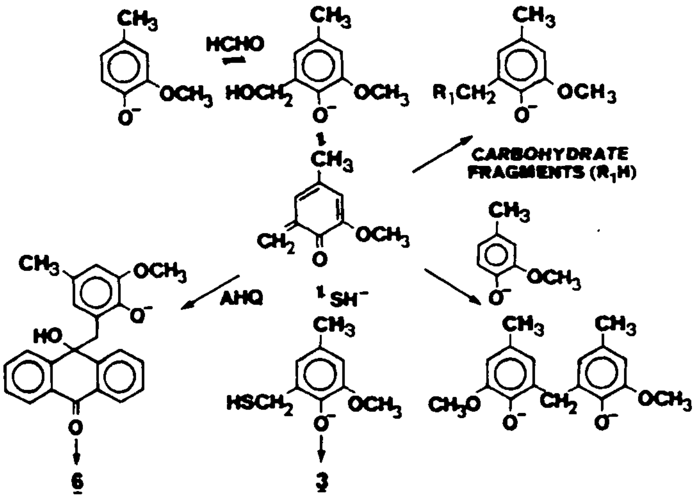


FIGURE 9 Alkaline reactions of 5-hydroxymethylcreosol.

the dimer even from 170°C cooks indicates that this may be a major cause of the slower rate of delignification in soda pulping. If this is so then modification of soda pulping conditions to minimize formaldehyde-promoted condensation reactions may lead to efficient alternatives to the kraft process for the production of chemical pulps. The use of 2,4- or 2,6-xylenol as a formaldehyde trap has already been reported[19].

As shown in Figure 9, the reactions of 5-hydroxymethylcreosol on alkali all center on the intermediate *o*-quinonemethide. In soda pulping, a coupling reaction with the phenoxide ion leads to the methylene-bridged dimer, but when hydrosulphide or anthrahydroquinone ions are also present, reaction with these nucleophiles is preferred.

In the kraft case, the initially-formed thiol reacts with a second *o*-quinonemethide leading to a sulphur-bridged dimer. This sulphur dimer was the major product at 135°C but was not found at 170°C; however, the lower yield of diphenylmethane dimer from kraft liquor at 170°C compared to soda indicates that the hydrosulphide ion is still limiting the extent of condensation. Presumably, besides reverting back to the o-quinonemethide, the intermediate sulphur dimer is also reacting further to other products.

Similarly, reduced forms of AQ have also been found to compete effectively with phenoxide ions for the o-quinonemethide. The resulting adduct (e.g., 6 in Fig. 9) may be reduced further to form the benzyl-substituted anthrone 7, particularly if large amounts of AHQ are present. In contrast to the sulphur dimer, both 6 and 7 are still detectable at 170°C. The reduction of the AQ adduct to its anthrone oxidation state may provide an explanation of how AQ is consumed during pulping because this step is irreversible, and results in AQ being removed from the catalytic cycle.

As also shown in Fig. 9 the intermediate o-quinonemethide may also react with carbohydrate degradation products. With a large excess of glucose this has been found to be a rapid reaction and very little dimer is formed whereas with bleached pulp at 135°C very little reaction occurs and the same amounts of starting material and dimer are obtained as in the soda control. The situation during pulping will be between these two extremes with the polymeric carbohydrates being slowly fragmented to release the reactive fragments which are then rapidly degraded. The influence of these carbohydrate components of the pulping liquor on lignin condensation reactions is difficult to predict. It is possible that such reactions may simply exchange the formation of alkali stable lignin-lignin bonds with lignin-carbohydrate ones which are equally resistant to alkaline degradation.

In considering the lignin condensation reactions that are likely to occur during pulping, it should be remembered that this study has deliberately been limited to a simplified lignin model in isolation. Other types of reactions of o-quinonemethide intermediates with parts of the lignin polymer have not been considered. An example is the recently reported reaction of an enol ether with an o-quinonemethide in a Diels Alder reaction to give a benzopyran product[20]. The formaldehyde may also add to the phenylpropane side chain of the lignin polymer.

In conclusion, this study has shown that 5-hydroxymethyl substituted lignins formed during pulping will be converted into o-quinonemethides and that the reactions of these intermediates may adversely affect pulping rates. Thus any modification of pulping conditions which limits either the release of formaldehyde or the reactivity of the 5-hydroxymethyl substituent may significantly enhance the rate of lignin removal.

EXPERIMENTAL

Compound 1 was readily synthesised by the reaction of creosol with formaldehyde as previously described[21] and was obtained as a stable colourless crystalline solid, 51-52°C (Lit[22] 50.5-51.5°C).

Reactions at 135°C

These reactions were done, normally in sets of six, by dissolving 5-hydroxymethylcreosol 1 (30 mg) in the pulping liquor (4 mL) in glass screw top reactors (5 mL capacity) and sealing them under nitrogen. The reactions tubes were then placed in a preheated oil bath at 135°C and heated for the required time.

Reactions at 170°C

These were done with the same quantities as above but using Teflon-lined stainless steel 10 mL bombs.

Pulping Liquors

The liquors used were 1N NaOH and white liquor (3.5 g NaOH + 3.1 g $Na_2S.9H_2O$ in 100 mL H_2O). For the AQ reactions commercial AQ powder was used.

Analytical Procedure

After reaction, the cooled solutions were diluted with water, acidified with 2N HCl and extracted with 3 x 8 mL of dichloromethane. The extract was filtered through anhydrous sodium sulphate and the filtrate and washings made up to 25 mL.

The solutions were analysed on a Varian Vista 5500 HPLC using a Whatman ODS-3 25 cm reverse-phase column at a flow rate of 1 mL/min and a 10 µL injection. The solvent gradient programme was 60:40 H_2O:MeOH for the first 7 min and then increasing to 100% MeOH by 20 min. The wavelength of the UV detector was set at 282 nm and the column temperature at 40°C. The internal standard was p-cresol and the response factors were determined as 0.61 for the starting material and creosol, 0.38 for the diphenylmethane 2 and the sulphur dimer 3, and 0.086 for the oxanthrone adduct 6. The value of 0.086 was also assumed for adduct 7 because this compound was not sufficiently stable to be obtained in a pure form.

The mass spectra were measured on an HP 5985 instrument using either an unheated direct insertion probe or by GC-MS of the trimethylsilylated derivatives (100 uL extract + 4 uL BSA) on a 30 m x 0.25 mm i.d. Durabond DB-17 fused silica capillary column wall coated (0.15 um film) with OV-17 (J & W Scientific). The temperature program was 60° for 1 min, 10°/min for 2 min and then 4°/min to 250°C. The proton nmr spectra were recorded on a Varian T60 spectrometer. The ^{13}C nmr spectra were recorded on a Bruker AC-200 FT nmr spectrometer.

Reaction in Sodium Hydroxide

The major product of this reaction was isolated as a colourless crystalline solid by prep. t.l.c. ($CHCl_3$) (Rf 0.25) and identified as the diphenylmethane dimer 2. Pmr δ ($CDCl_3$) 2.24 (6,s,$ArCH_3$), 3.85 (6,s,$ArOCH_3$), 3.93 (2,s,$ArCH_2Ar$), 5.92 (2,brd.s,phenolic OH), 6.55 and 6.60 (4,2s, C-2 and C-6 aromatic protons). ^{13}C nmr δ ($CDCl_3$) 21.17 ($ArCH_3$), 29.24 ($ArCH_2Ar$), 56.01 ($ArOCH_3$), 109.95 (C-2), 122.92 (C-6), 126.32 (C-5), 129.06 (C-1), 140.91 (C-4), 146.49 (C-3). M.S. (m/e) 288 (M^+) (70), 255 (12), 151 (40), 150 (28), 149 (10), 138, (100).

Reaction in Kraft Liquor

The main product from the reaction in kraft liquor at 135°C was identified as the sulphide dimer 3. This was obtained by prep. t.l.c. ($CHCl_3$:EtOAc 9:1) (Rf 0.5) as a colourless oil which slowly decomposed on standing. Pmr δ ($CDCl_3$) 2.26 (6,s,$ArCH_3$), 3.75 (4,s,$ArCH_2S$), 3.85 (6,s.$ArOCH_3$), 5,72 (2,s,phenolic OH), 6.59 and 6.67 (4,2s,C-2 and C-6 aromatic protons). ^{13}C nmr δ ($CDCl_3$) 21.10 ($ArCH_3$), 30.55 ($ArCH_2SCH_2Ar$), 56.05 ($ArOCH_3$), 110.66 (C-2), 122.89 (C-6), 126.31 (C-5), 128.86 (C-1), 141.52 (C-4), 146.47 (C-3). M.S. (m/e) 334 (M^+) (34), 184 (37), 152 (41), 151 (100), 150 (87), 136 (8), 123 (7), 121 (14), 107 (15), 91 (14), 79 (21), 77 (26).

Also tentatively identified in this reaction mixture were 5-thiomethylcreosol 4 (prep. t.l.c. Rf 0.6), M.S. (m/e) 184 (M^+) (28), 173 (6), 167 (10), 159 (12), 155 (5), 151 (25), 150 (29), 149 (36), 138 (12), 123 (15), 121 (12), 71 (100), and the disulphide bridged dimer 5, M.S. (m/e) 366 ($M^{+\cdot}$) (8), 151 (100), as well as creosol and the non-sulphur dimer 2.

Reaction With Oxanthrone

Preparative t.l.c. of the products from the reaction of 5-hydroxymethylcreosol with oxanthrone in $CHCl_3$ gave a fraction (Rf 0.6) which contained a mixture of the oxanthrone and anthrone adducts 6 and 7.

10-Hydroxy-10-(2-hydroxy-3-methoxy-5-methylbenzyl)-9(10H) anthracenone 6. Pmr δ ($CDCl_3$) 1.96 (3,s,$ArCH_3$), 3.21 (2,s,$ArCH_2$), 3.68 (3,s,$ArOCH_3$), 4.78 (1,s,phenolic OH), 5.49 (1,brd.s, C-6 aromatic proton), 6.38 (1,brd.s, C-2 aromatic proton), 7.42-8.35 (8,m,AQ protons). M.S. (m/e) 360 ($M^{+\cdot}$) (2), 359 (4), 358 (14), 210 (100), 209 (42), 181 (8), 180 (6), 153 (14), 152 (58), 151 (28), 149 (27), 77 (20).

10-(2-hydroxy-3-methoxy-5-methylbenzyl)-9(10H)-anthracenone 7. Pmr δ ($CDCl_3$) 2.01 (3,s,$ArCH_3$), 2.92 (2,d,J = 7Hz), 3.81 (3,s,$ArOCH_3$), 4.51 (1,t,C-10 proton, J = 7Hz) 5.39 (1,s,ArOH), 5.71 (1,brd.s, C-6 aromatic proton), 6.46 (1,brd.s, C-2 aromatic proton), 7.08-7.48 and 7.86-8.2 (anthrone protons). ^{13}C nmr δ ($CDCl_3$) 20.93 ($ArCH_3$), 43.59 (C10), 44.63 ($ArCH_2$), 56.10 ($ArCH_3$), 110.29 (C2'), 123.85 (C5'), 124.39 (C6'), 126.93 (C2, C7), 127.22 (C1, C8), 128.22 (C1'), 132.02 (C8a, C9a), 132.17 (C3, C6), 141.82 (C4'), 145.25 (C4a, C10a), 146.03 (C3'), 185.02 (C9). M.S. (m/e) 344 ($M^{+\cdot}$), 195, 194 (100), 193, 151, 123, 108.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to PAPRICAN for the award of the Gendron Fellowship and his thanks to Drs H.I. Bolker, B.I. Fleming, R.D. Mortimer and R.M. Berry and the many others at the Institute who provided the assistance and support which made this work possible. Special thanks to Mr P.Y. Wong for his assistance with the HPLC studies.

REFERENCES

1. J. Martin, Lignins, Chap. 16, K.V. Sarkanen and E.H. Ludwig (eds.), Wiley Interscience, New York, 1971.
2. E.Hägglund, Svensk Papperstidn., 44, 183 (1941).
3. J.R. Obst, L.L. Landucci and N.Sanyer, Tappi, 62 (1), 55 (1979).
4. H. Aminoff, G. Brunow, G.E. Miksche and K. Poppinus, Paperi ja Puu, 61, 441 (1979).
5. D.R. Dimmel, D. Shepard and T.A. Brown, J. Wood Chem. Tech., 1 (2), 123 (1981).
6. N. Terashima, H. Araki and N. Suganuma, Mokuzai Gakkaishi, 23 (7), 343 (1977).
7. G. Gellerstedt and E.L. Lindfors, Holzforschung, 38 (3), 151 (1984).
8. J. Gierer, Svensk Papperstidn., 73, 571 (1970).
9. J. Ralph and R.M. Ede, Proceedings Internat. Symp. Wood and Pulping Chem., Vancouver, p. 83 (1985).
10. S. Yasuda, B-H. Yoon and N. Terashima, Mokuzai Gakkaishi, 26, (6), 421 (1980).
11. K. Hästbacka, Paperi ja Puu, 43 (11), 665 (1961).
12. T. Enkvist, T. Ashorn and K. Hästbacka, Paperi ja Puu, 44 (8), 395 (1962).
13. D.A. Smith and D.R. Dimmel, Proceedings Internat. Symp. Wood and Pulping Chem., Vancouver, Posters p. 39 (1985).
14. K.L. Brown and T.J. Fullerton, Acta Crystallographica, B36 (12), 3199 (1980).
15. D.R. Dimmel and D. Shepard, J. Wood Chem. Tech., 2 (1), 73 (1982).
16. T.J. Fullerton, J.A. Hemmingson, G.J. Leary and L.J. Wright, J. Wood Chem. Tech., 2 (1), 97 (1982).
17. T.J. Fullerton and L.J. Wright, Tappi, 67 (3), 78 (1984).
18. T.J. Fullerton and A.L. Wilkins, J. Wood Chem. Tech., 5 (2), 189 (1985).

19. J. Gierer and O. Lindeberg, Acta Chem. Scan., B33, 580 (1979).

20. A. Arduini, A. Bosi, A. Pochini and R. Ungaro, Tetrahedron, 41 (15), 3095 (1985).

21. J. Marton, T. Marton, S.I. Falkehag and E. Adler, Advances in Chem. Series, 59, 125 (1966).

22. J. Gierer, J. Lenic, I. Noren and I. Szabo-Lin, Acta Chem. Scan., B28 (7), 718 (1974).