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THE MODIFICATION OF LIGNIN AT POSITIONS 2 AND 6 OF THE
PHENYLPROPANOID NUCLEI - PART III:
HYDROXYMETHYLATION OF INDUSTRIAL LIGNIN

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ABSTRACT

Three alkali lignins from different industrial origins were reacted with formaldehyde under acidic conditions. Depending on the conditions, the lignins were crosslinked and hydroxymethylated at positions 2 and 6 on the lignin phenylpropanoid units.

INTRODUCTION

Large quantities of lignin are produced by chemical pulping as an underutilized by-product. During the pulping process, the lignin macromolecule is degraded to give water soluble fragments which can be removed from the pulp by washing. The degraded lignin nevertheless still has a polymeric character which prompted research into its utilization in polymeric products. However, to date, only limited success has been achieved. This can be attributed to various inherent properties of the industrial by-product lignin, such as the randomness of the inter-unit linkages and the three-dimensional character of lignin. One very important property, though, is the low number of sites available for modification on industrial lignin,

particularly since most polymeric applications of lignin use unsubstituted 3- or 5-positions for modification. These positions are usually available only in small proportions, particularly owing to their substitution by condensation reactions occurring during pulping.

Recently it was shown with model compound experiments that the 2- and 6-positions on the aromatic nuclei of lignin can be crosslinked with formaldehyde¹. Subsequent research showed that under appropriate conditions, these positions, which are situated meta to the aromatic hydroxy group, can be hydroxymethylated in high yield². The introduced meta hydroxymethyl groups have a high reactivity towards nucleophiles in acidic aqueous media¹. The meta hydroxymethylation of lignin therefore has the potential of transforming industrial lignins into reactive intermediates useful in polymeric applications.

In this paper, the suitability of the different conditions found for the hydroxymethylation of model compounds were evaluated on three alkali lignins obtained from different industrial spent liquors.

DISCUSSION

The alkali lignins used were selected from different industrial origins in order to have a wide variation in their properties. The lignins were a kraft softwood, soda/AQ hardwood and soda bagasse lignin (Table 1).

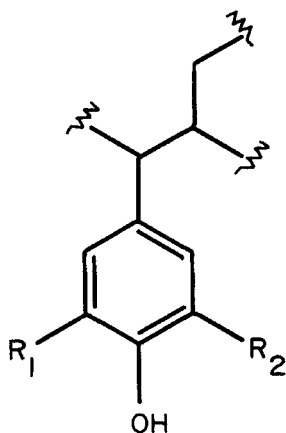
The kraft lignin is constituted mainly of guaiacylpropanoid units (2) of which about half are condensed, i.e. substituted at the 5-position³. The number of aromatic sites reactive towards base catalysed electrophilic substitution reactions therefore is fairly low at about 0,3 per C₉ unit (Table 1).

TABLE I
Properties of Three Industrial Lignins^{3,4,5}

LIGNIN	TYPE	PLANT MATERIAL	NUMBER OF PHENOLIC GROUPS/C ₉ ^a	NUMBER OF UNSUBSTITUTED 3/5 POSITIONS (C ₉) ^b	CALCULATED NUMBER OF UNSUBSTITUTED 3/5 POSITIONS ON AROMATIC RINGS (C ₉)	AVERAGE MOLECULAR MASS (C ₉)	DEGREE OF POLYMERIZATION (MOLECULAR MASS/M _n)
Kraft	Softwood	Pine	0,63	0,48	0,3	176	5,7
Soda/AQ	Hardwood	Eucalyptus	0,77	0,10	0,1	184	6,1
Soda	Grass	Bagasse	0,63	1,05	0,7	175	6,3

a = Determined by ¹H-NMR analysis of acetylated lignin^{3,4,5}

b = Determined by ¹H-NMR^{3,4,5}



- 1** : $R_1 = R_2 = \text{H or } -\text{Z}$
2 : $R_1 = \text{H or } -\text{Z}, R_2 = \text{OMe}$
3 : $R_1 = R_2 = \text{OMe}$

$-\text{Z}$ = POSSIBLE LINKAGE TO OTHER
 PHENYL PROPANE UNITS

FIGURE 1 PHENYLPROPANOID BUILDING UNITS OF LIGNIN

The soda/AQ hardwood lignin is constituted of both guaiacyl (2) and syringylpropanoid (3) units of which the former have been condensed extensively during pulping⁴. This is indicated by the low number of unsubstituted 5-positions. (Table 1).

The soda bagasse lignin, on the other hand, is an extremely reactive industrial lignin as is indicated by its high number of unsubstituted 3- and 5-positions of 0,7/C₉. This lignin is only

TABLE 2

The Reaction of 4-Hydroxy-3,5-Dimethoxyphenyl Ethane (**4**) with Formaldehyde in Acidic Aqueous Dioxane at 80 °C^{1,2}

MOLE H ₂ CO/ MOLE 4	SOLVENT	[H ⁺]	Temp. (°C)	TIME (h)	PRODUCT
1 : 1	50 % aq dioxane	2,2 N HCl	80	≈ 6	Mainly methylene linkages. No hydroxymethylated compounds were isolated
1 : 2	23 % aq dioxane	1,0 N HCl	80	≈ 6	100 % Monohydroxymethylation + 20 % methylene linkages
1 : 2	10 % aq	0,4 N HCl	80	6	100 % Monohydroxymethylation

mildly condensed and contains 1,05 unsubstituted 3- or 5-positions.

The alkali lignins were reacted with formaldehyde in acidic dioxane solutions according to procedures established previously by model compound experiments^{1,2}. The results of the model compound investigations are summarised in Table 2. Clearly the degree of meta hydroxymethylation versus methylene linkage formation of **4** can be controlled in either direction (Fig. 2). Phenolic and non-phenolic softwood as well as non-phenolic hardwood model compounds gave similar products^{1,2}.

The industrial lignins were reacted with an excess formaldehyde of 1,35 mole H₂CO/mole C₉ of each lignin. When the reactions were performed in 2,2 N hydrochloric acid in 50 % aqueous dioxane, the lignins polymerized as expected. The polymerization

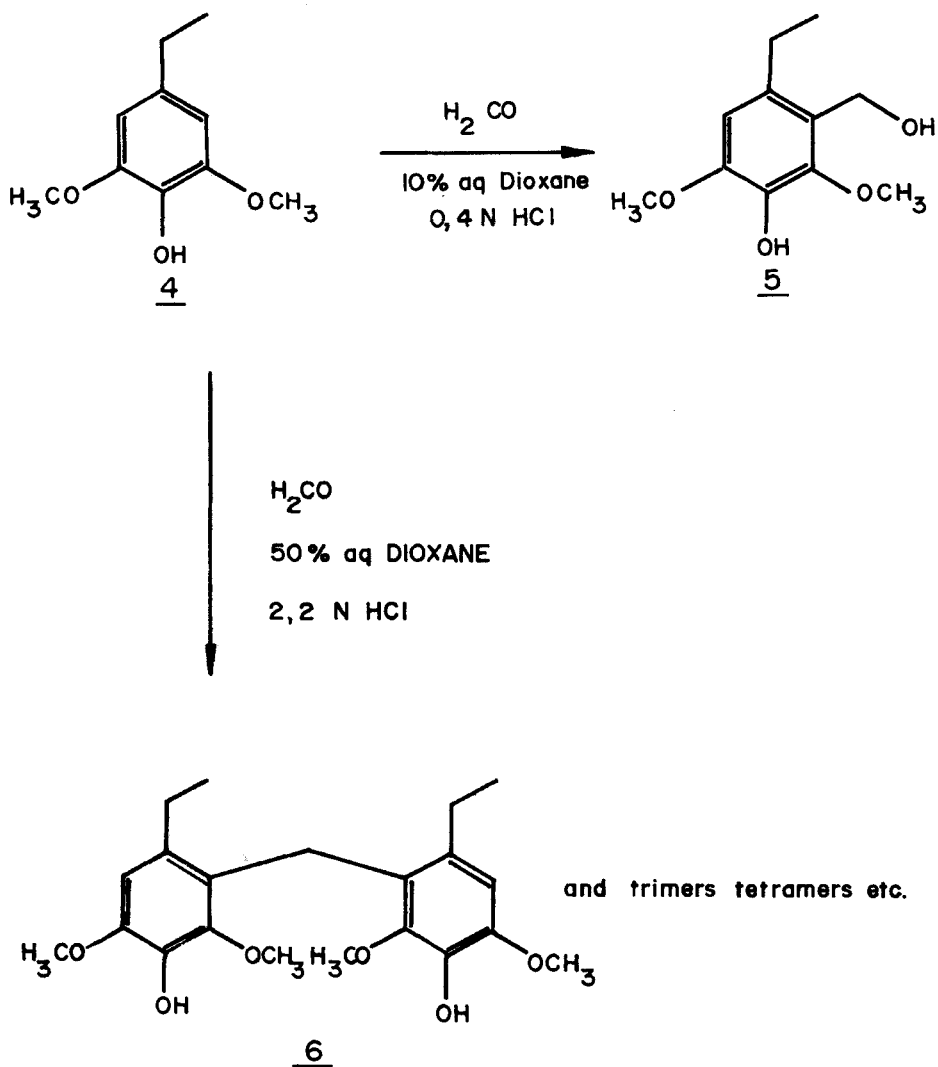


FIGURE 2: The Reaction of 4-Hydroxy-3,5-Dimethoxyphenyl Ethane (4) With Formaldehyde in Acidic Aqueous Dioxane^{1,2}

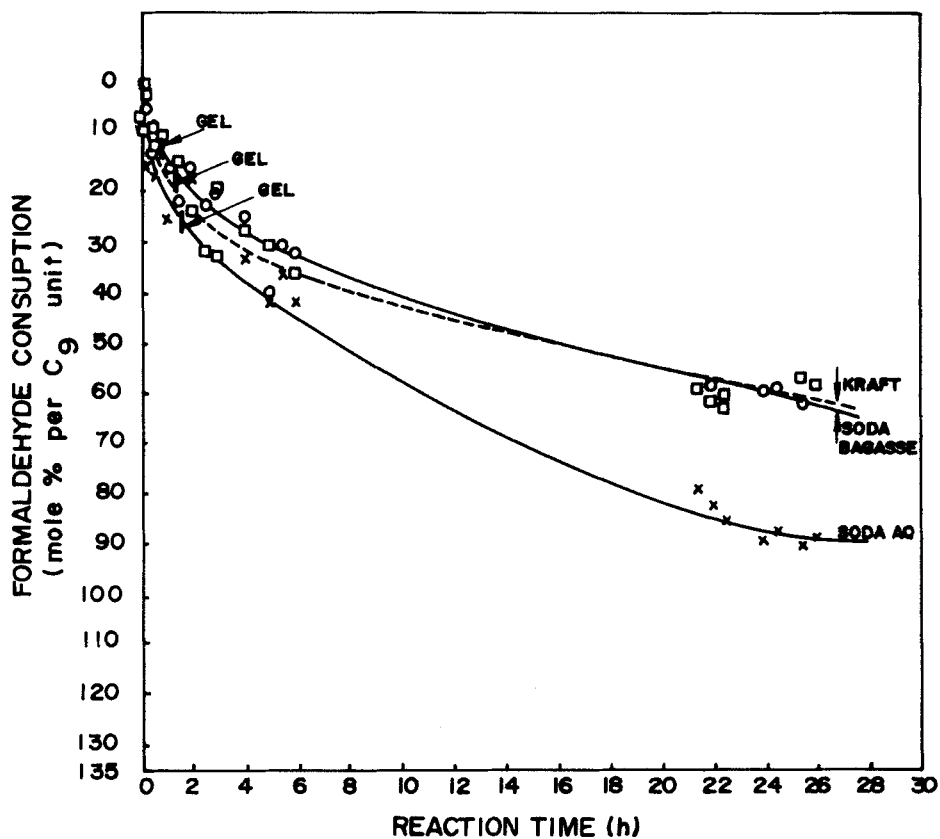


FIGURE 3 REACTION OF LIGNINS WITH FORMALDEHYDE IN 50 % AQUEOUS DIOXANE AT 80 °C

occurred only after a small proportion of the formaldehyde had reacted (Fig. 3) indicating that extensive methylene linkage formation (crosslinking) occurred. After gelling of the lignins had occurred, formaldehyde was still consumed by the crosslinked lignins though at a lower rate. The latter portion of formaldehyde can be expected to result in further methylene linkage formation or in hydroxymethylation of the lignin fragments if steric hindrance prevents the formation of methylene linkages.

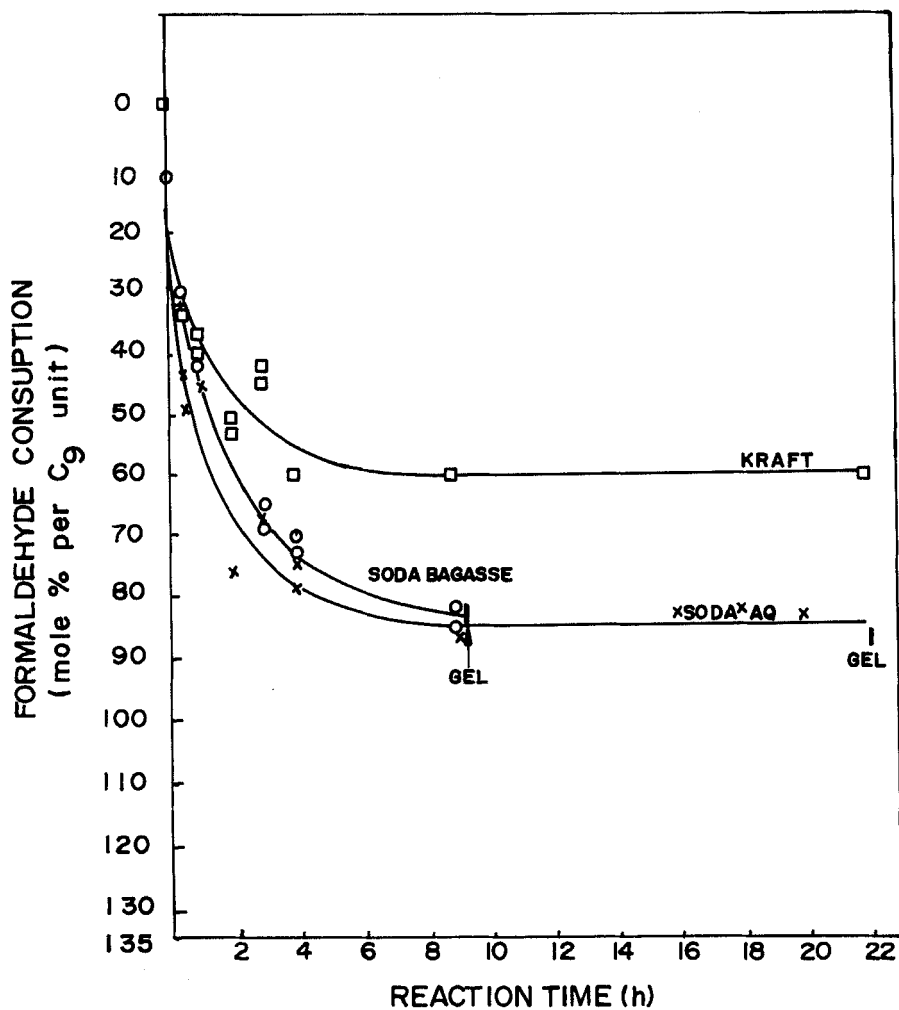


FIGURE 4 REACTION OF LIGNIN WITH FORMALDEHYDE IN 0,4 N HYDROCHLORIC ACID IN 10 % AQUEOUS DIOXANE AT 80 °C

Each lignin was subsequently reacted with formaldehyde in 10 % aqueous dioxane containing 0,4 N hydrochloric acid (Fig. 4). Under these conditions, only mono meta hydroxymethylation is expected. The soda bagasse and soda/AQ lignin reacted very fast and consumed about half of the theoretical amount of formaldehyde in one hour. The rate of formaldehyde consumption levelled off after about 5 hours. The total quantity consumed for both the soda/AQ and soda bagasse lignin is approximately 85 % of the calculated theoretical amount. The formaldehyde consumed by the kraft lignin levelled off after 60 % of the stoichiometric calculated quantity had been consumed. Some crosslinking of the lignin, however, still occurred since the soda bagasse lignin gelled after ca 9 hours and the soda/AQ lignin after 20 hours. The kraft lignin showed no gelling after 28 hours reaction time. The results obtained nevertheless show that lignin can be extensively meta hydroxymethylated without crosslinking. Prolonged reaction times should, however, be excluded.

The high formaldehyde consumption by the bagasse lignin can probably be attributed to mono-hydroxymethylation of syringyl (3) and guaiacyl (2) phenylpropanoid units at the 2- and 6-positions. The para hydroxyphenyl (1) units of the lignin were probably hydroxymethylated at the ortho (3- or 5-) positions. The formaldehyde consumption of the soda/AQ lignin can only be attributed to meta hydroxymethylation, owing to the low availability of unsubstituted 5-positions. The extensive consumption of formaldehyde by this lignin and its unpolymerized state after 6 hours thus clearly indicates that meta hydroxymethylation of the lignin was achieved in high yield.

The industrial lignins were each also reacted with formaldehyde in 23 % aqueous dioxane and 1,0 N hydrochloric acid (Fig. 5). The soda/AQ and soda bagasse lignin again consumed

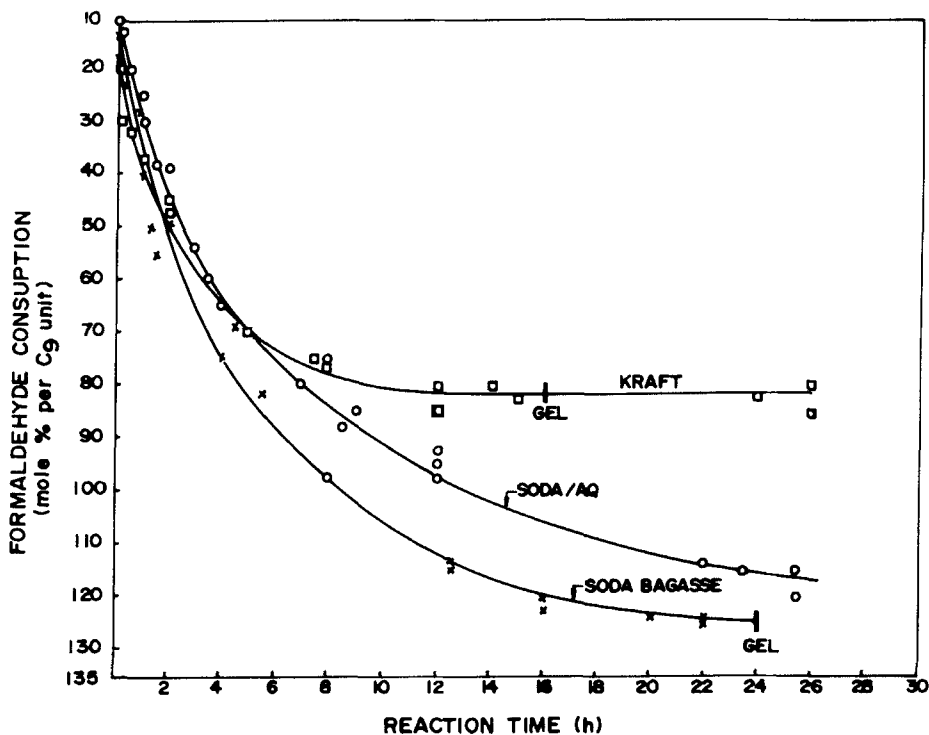


FIGURE 5 REACTION OF SODA BAGASSE LIGNIN WITH FORMALDEHYDE IN 1,0 N HYDROCHLORIC ACID IN 23 % AQUEOUS DIOXANE AT 80 °C

more formaldehyde when compared with the kraft lignin. The total consumption for each lignin is more than that observed in 10 % aqueous dioxane (Fig. 4). This can probably be explained by the formation of methylene linkages in addition to almost 100 % mono-hydroxymethylation which was previously observed for the model compound 4 (Table 2)². The number of methylene linkages formed must be low since the lignins did not gel.

The kraft lignin consumed less formaldehyde in both 10 % and 23 % aqueous dioxane solutions than the soda/AQ lignin. The

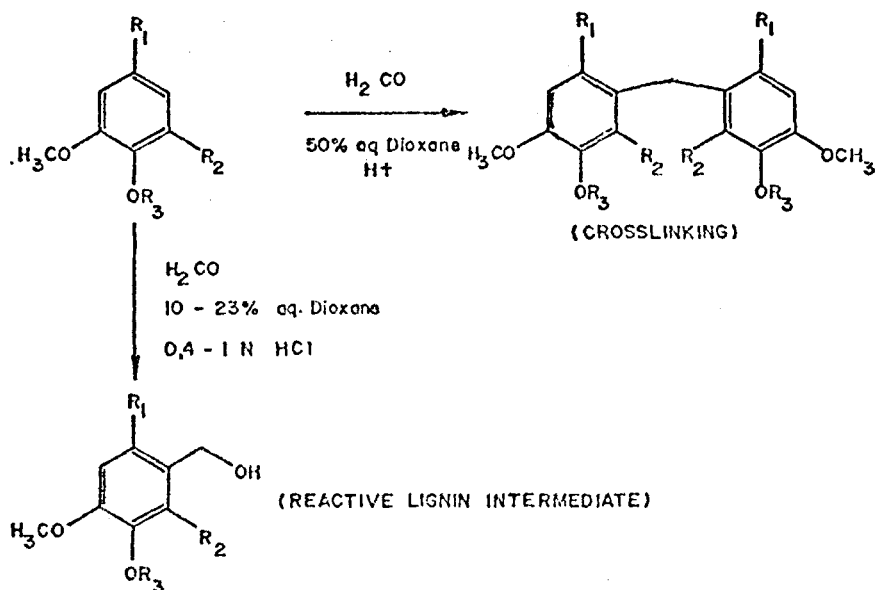


FIGURE 6 GENERALIZED REACTION OF FORMALDEHYDE WITH LIGNIN AT THE META POSITIONS IN ACIDIC AQUEOUS DIOXANE
 R_1 = ALKYL LIGNIN FRAGMENT; R_2, R_3 = H OR LIGNIN FRAGMENT

lower reactivity of the kraft lignin could be caused by the presence of deactivating groups on the α position of the kraft lignin side chains such as a hydroxy or a ether groups. The soda/AQ lignin can be expected to contain less of these groups since it is an extensively condensed lignin and should therefore contain less α oxy-moieties.

The reactions applied above can be generalised as follows: In 50 % aqueous dioxane and acidic conditions, lignin reacts with formaldehyde at positions 2- and 6- to give methylene crosslinks which result in the formation of a gelled or polymerized product (Fig. 6).

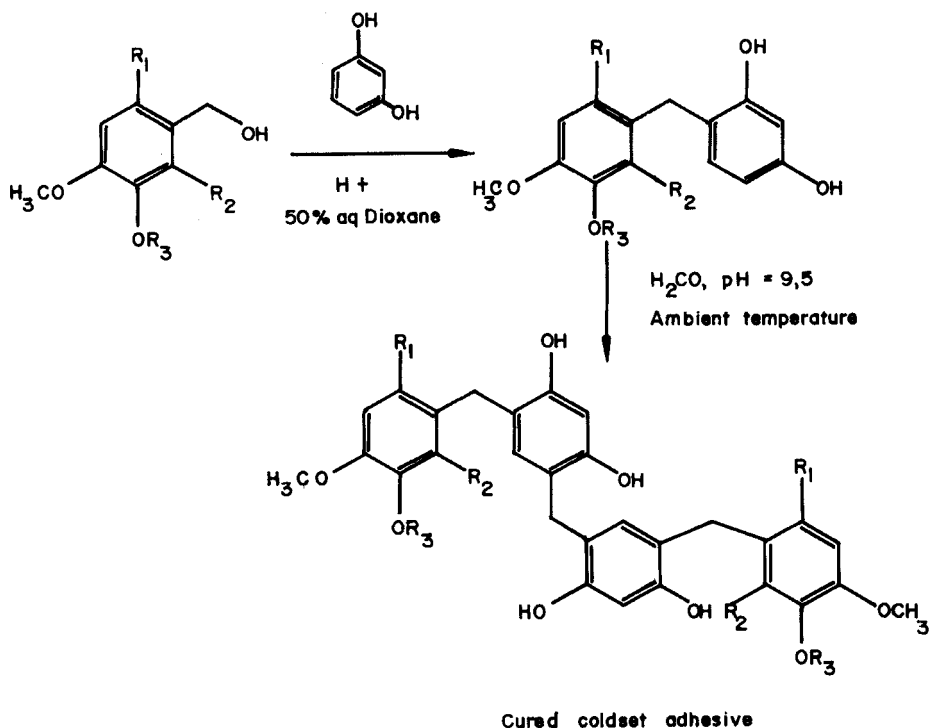


FIGURE 7 DIAGRAMMATIC ILLUSTRATION OF THE UTILIZATION OF THE META-HYDROXYMETHYLATION OF LIGNIN FOR THE PRODUCTION OF COLD SET WOOD ADHESIVES

In 10 to 20 % aqueous dioxane containing 0,4 to 1 N hydrochloric acid, meta hydroxymethylation occurs preferentially. This results in the creation of a reactive intermediate capable of being modified with various reagents or by reacting with itself.

The exploitation of the meta hydroxymethylation of lignin was taken one step further. Meta-hydroxymethylated kraft lignin (10 % aqueous dioxane, 0,4 HCl for 16 hours) was neutralized and washed in order to remove any excess formaldehyde. The reactive

lignin intermediate was reacted with resorcinol (0,39g/g lignin) in 50 % aqueous dioxane at ambient temperature for 2 hours. The solution was neutralized and the lignin resorcinol adduct filtered after addition of additional water, followed by proper washing in order to remove unreacted resorcinol. The purified lignin-resorcinol adduct was alkalified to $\text{pH} \approx 10$ and paraformaldehyde added resulting in soft gelling of the product in about 6 minutes. The polymerized product was hard and resisted solvation in sodium hydroxide solutions. This result indicates some potential of the meta-hydroxymethylation of lignin to result in the production of, for example, cold set wood adhesives. Figure 7 explains the above experiment diagrammatically.

EXPERIMENTAL

Reaction of Formaldehyde with Lignin in Acidic Aqueous Dioxane

The purification of the industrial kraft pine, soda/AQ eucalyptus and soda bagasse lignins are described elsewhere^{3,4,5}. Lignin samples (20 g) were added to 50, 23 and 10 % aqueous dioxane solutions (80 ml) at $80 \pm 0,5^\circ\text{C}$ containing 2,2, 1,0 or 0,4 N hydrochloric acid and paraformaldehyde. An excess of 1,35 moles of formaldehyde/mole C_9 unit of each lignin (Table 2) was used. The formaldehyde consumption was determined by the ammonium-hydrochloride method⁶ and is listed in Figures 3, 4 and 5.

Kraft Lignin-Resorcinol Adduct

Kraft lignin (100 g) was reacted with formaldehyde (10 g) in 10 % aqueous dioxane (500 ml) containing hydrochloric acid (0,4

N) at 80 °C for 4 hours. The mixture was neutralised to pH \approx 3 with NaHCO₃ and acetic acid. Half of the dioxane was evaporated under reduced pressure. The remaining mixture was diluted with water (ca 500 ml) and the lignin precipitate filtered. After washing (3 x 300 ml water) a portion of the lignin precipitate (30 g, 29,2 % solids) was reacted with resorcinol (3,0 g) in 50 % aqueous dioxane (100 ml) and 1,0 N hydrochloric acid at ambient temperature for 4 hours.

The product was suspended in water (300 ml), filtered and washed (2 x 50 ml water) to remove unreacted resorcinol. The purified lignin- resorcinol adduct was alkalified to pH \approx 10 with sodium hydroxide and formaldehyde (1,0 g) added.

ACKNOWLEDGEMENTS

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