

# Cold-Setting Wood Adhesives from Kraft Hardwood Lignin

P. TRUTER,<sup>1,\*</sup> A. PIZZI,<sup>2</sup> and H. VERMAAS<sup>3</sup>

<sup>1</sup>Division of Materials Science and Technology, CSIR, Pretoria, South Africa; <sup>2</sup>University of the Witwatersrand, Johannesburg, South Africa; <sup>3</sup>University of Stellenbosch, Stellenbosch, South Africa

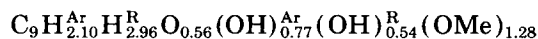
## SYNOPSIS

The model compound used in this study, for hardwood kraft lignin, 3,5-dimethoxy-4-hydroxyphenyl ethane, was successfully hydroxymethylated at the position *meta* to the aromatic hydroxy group. The consequent expectation that kraft hardwood lignin syringyl units can, under optimum conditions, also be hydroxymethylated to a substantial extent was confirmed in the present work and made it possible to cross-link the kraft hardwood lignin to yield polymeric products that could be used as adhesives. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The objective of this investigation was the evaluation of hardwood kraft lignin as a basis for the preparation of a wood adhesive. It was shown with the model compound experiments that the 2- or 6-positions of the aromatic nuclei of the hardwood kraft lignin can be hydroxymethylated. The introduced hydroxymethyl groups provide the potential of transforming industrial hardwood kraft lignins into reactive intermediates useful in polymeric applications such as adhesives.

Kraft hardwood lignin has the following molecular formula:



It is reputed to have low reactivity toward formaldehyde, due to its predominant proportion of syringyl propane units<sup>1</sup> (Fig. 1.). This limits the possibility of formaldehyde attack at the 3- and 5-positions of the aromatic nuclei, sites mostly occupied by methoxy groups (see molecular formula). Recently, the possibility of formaldehyde attack at the 2- and 6-positions on hardwood lignin model compounds has been proposed in a reaction conducted in dioxane.<sup>2</sup>

Dioxane is a relatively expensive and toxic solvent. The LD<sub>50</sub> oral for rats is 6 g/kg,<sup>3</sup> and the lethal concentration in air is 5000 ppm—even at much lower concentrations, the vapor is harmful. Dioxane is, therefore, unsuitable for commercial formulations. Many other solvents including water, methanol, acetone, toluene, and pyridine and their mixtures were tried for the reaction, but without success. Tetrahydrofuran, however, was found to be suitable for both hydroxymethylating kraft wood lignin as well as for grafting resorcinol onto it.

Tetrahydrofuran has a threshold limit value (TLV) of 25,000 ppm in air (8 h daily exposure) and has been accepted in the U.S. Federal Food, Drug and Cosmetic Act for fabrication of articles for packaging, transporting, or storing of foods if the residual amount does not exceed 1.5% of the film.<sup>3</sup> Furthermore, tetrahydrofuran is much cheaper than dioxane, creating the possibility for the manufacture of a cold-setting wood adhesive based on the reaction of tetrahydrofuran and industrial wood lignin. The current article covers

- the reaction of hardwood lignin model compounds with formaldehyde and resorcinol in tetrahydrofuran to form lignin model/formaldehyde/*d*-resorcinol adducts, and
- the novel preparation of resins similar to the model compound adduct to form kraft hardwood lignin-based cold-setting wood adhesives.

\* To whom correspondence should be addressed.

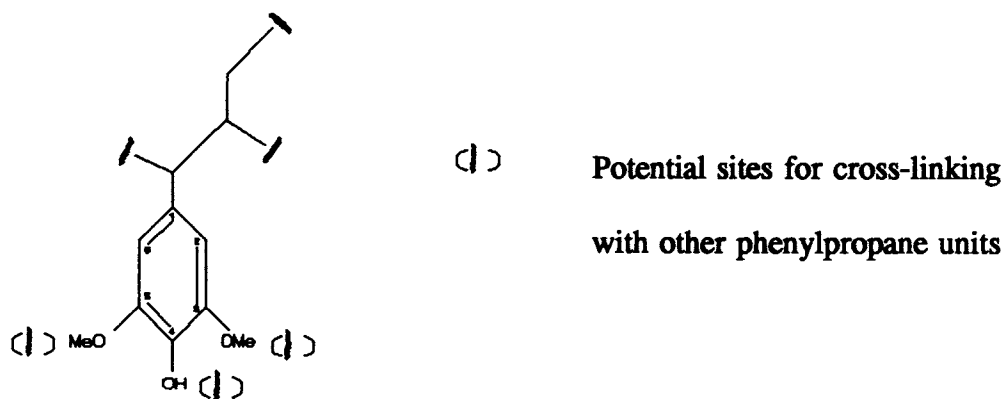


Figure 1 Schematic formula for kraft hardwood lignin.

## EXPERIMENTAL

### Synthesis of Model Compounds (See Reaction Schematic: Fig. 2)

#### Synthesis of Model Compound Adduct I

3,5-Dimethyl-4-hydroxyphenyl ethane (**0**), 0.5 g, and 0.0824 g paraformaldehyde 96% (powder) in 10 mL tetrahydrofuran containing 0.625 g concn HCl were refluxed 24 h at 66°C. The cooled mixture was dried over sodium sulfate and filtered and the solvent evaporated. The product was flash-chromatographed on Merck Kieselgel 60 (0.063–0.200 mm) with ethyl acetate : hexane 1 : 1 to afford pure 2-hydroxymethyl 3,4-dimethoxy-4-hydroxyphenyl ethane (**I**). Spectra were obtained in acetone- $d_6$ .

#### Synthesis of Model Compound Adduct II

2-Hydroxymethyl 3,4-dimethoxy-4-hydroxyphenyl ethane (**I**), 0.5 g, and 0.3022 g resorcinol in 10 mL

tetrahydrofuran and 10 mL water containing 1.25 g concn HCl were refluxed for 3 h. The mixture was extracted with ether twice, washed with water, and dried over sodium sulfate and the ether evaporated and the product flash-chromatographed on Merck Kieselgel 60 with ethylacetate : hexane 1 : 1 eluent. Spectra were obtained in acetone- $d_6$ .

#### Synthesis of Hardwood Kraft Lignin/ Formaldehyde/ Resorcinol Cold-set Wood Adhesives

Kraft hardwood lignin powder, 100 g, in 200 g tetrahydrofuran and 26.52 g of 32% HCl were reacted with 17.76 g paraformaldehyde (96%) powder at 60°C for 24 h. Resorcinol in amounts of 43.74, 48.12, or 52.8 g in 180 g water was added to the reaction mixture and reacted at 25°C for 2 h. The pH was adjusted to 6 with 40% NaOH and the tetrahydrofuran evaporated in a rotary evaporator. The pH was adjusted to 9.5, again with 40% NaOH. Thirty

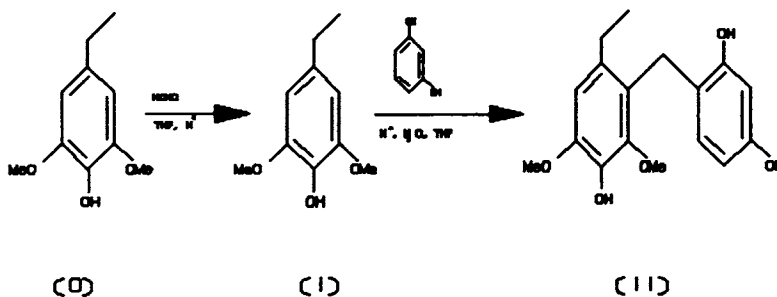


Figure 2 Reaction schematic: The synthesis of model compound adduct (**I**) and (**II**) from 3,5-dimethyl-4-hydroxyphenyl ethane (**0**).

**Table I**  $^1\text{H-NMR}$  Chemical Shifts (ppm) for Model Compound Adduct I in Acetone- $d_6$ 

Site	Shift	Multiplicity
3H, (CH—CH)	1,2	t
1H, (Ar—H)	1,58	s
1H, (CH—OH)	2,15	s
2H, (CH—CH)	2,59	q
6H, (2 X O—CH)	3,85	s
1H, (Ar—OH)	5,33	s
2H, (CH—OH)	6,4	s

s = singlet; t = triplet; q = quartet.

percent of methanol was then added to vary the % solids content of the resin solution. To 50 g of the adhesive resin solution thus formed were added 14.21 g paraformaldehyde (96%) powder, 0.7 g macadamia nut flour filler (200 mesh), and 1.4 g wood flour filler (200 mesh). Beech strips were then bonded with this glue mix according to British Standard BS 1204-1965, Part 2, for close contact adhesive resins for wood<sup>4</sup> and cured at 25°C, 12% equilibrium moisture content (e.m.c.) for 7 days.

## RESULTS

For results, see Tables I–IV.

## DISCUSSION

The yield of 2-hydroxymethyl-3,4-dimethoxy-4-hydroxyphenyl ethane (I) depended on the normality

**Table II** Infrared Spectra of Model Compound Adduct I

Site (Group)	Wavenumber (cm <sup>-1</sup> )
—OH	3500 (broad)
—CH	3000, 2900, 2800
—CH—	1610
C=C (Ar)	1520
—CH	1490
—OH	1420 (sharp)
—CH—CH	1350

**Table III**  $^1\text{H-NMR}$  Chemical Shifts (ppm) for Model Compound Adduct II in Acetone- $d_6$ 

Site	Shift	Multiplicity
3H, (CH—CH)	1,20	s
2H, (CH—CH)	2,50	q
1H, (Ar—H)	3,35	s
6H, (2 X O—CH)	3,85	s
2H, (Ar—CH—Ar)	3,90	s
1H, (Ar—H)	6,20	d
1H, (Ar—OH)	6,30	s
1H, (Ar—H)	6,35	d
1H, (Ar—OH)	6,60	s
1H, (Ar—OH)	7,25	s
1H, (AR—H)	7,85	s

s = singlet; d = doublet; q = quartet.

of the HCl in the mixture. Yields were 62% (0.25N HCl), 85% (0.5N HCl), 52% (1.0N HCl), and 4% (2.0N HCl). HCHO uptake by the model compound to form (I) and the corresponding HCHO uptake of kraft hardwood lignin are shown in Table V.

## CONCLUSIONS

The model compound used for hardwood kraft lignin, 3,5-dimethoxy-4-hydroxy-phenyl ethane, was successfully hydroxymethylated at the position *meta* to the aromatic hydroxyl group. The consequent expectation that kraft hardwood lignin syringyl units can, under optimum conditions, also be hydroxymethylated to a substantial extent was confirmed. This made it possible to cross-link the kraft hardwood lignin to yield polymeric products that can be used as adhesives.

**Table IV** Infrared Spectra of Model Compound Adduct II

Site (Group)	Wavenumber (cm <sup>-1</sup> )
—OH	3400 (broad)
—CH	2900, 2850, 2750
—CH—	1705
C=C (Ar)	1620
—CH	1500
—OH	1420
—CH—CH	1380

**Table V Formaldehyde Uptake<sup>a</sup> by the Model Compound and the Kraft Hardwood Lignin**

Time (h)	Uptake by Model Compound (%)	Uptake by Kraft Hardwood Lignin (%)
0.5	19	2
1	37	7
3	51	29
6	73	37
18	89	47
Asymptote	≈ 100	≈ 55

<sup>a</sup> Amount of HCOH added corresponded to 100% of stoichiometric requirements. The incomplete uptake of HCHO by the lignin is attributed to steric hindrance.

**REFERENCES**

1. K. W. Sarkanen and H. K. Hergert, in *Lignins, Occurrence, Formation, Structure and Reactions*, K. W. Sarkanen and C. H. Ludwig, Eds., Wiley-Interscience, New York, 1971.
2. G. van der Klashorst and A. Pizzi, 1989, in *Wood Adhesives Chemistry and Technology*, A. Pizzi, Ed., Marcel Dekker, New York, Chap. 6.
3. M. Windholz, Ed., *An Encyclopaedia of Chemicals and Drugs*, 9th ed., Merck, Rahway, NY, 1976.
4. British Standard BS 1204-1956, Part 2, Standard specification for adhesive resins for wood, close contact adhesives, 1956.

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