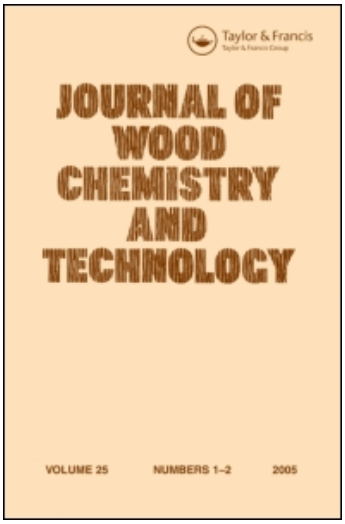

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Fractionation-Purification, IR, ^{1}H ^{13}C NMR Spectral and Property Studies of an Industrial Based Sludge Lignin

Roger D. McElroy[ab]; Ky Lai[a]
[a] Mississippi Forest Products Laboratory, Mississippi State University, Mississippi State, Mississippi [b] Department of Agriculture and Industries, Chemistry Laboratory, Montgomery, AL

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FRACTIONATION-PURIFICATION, IR, ^{1}H NMR, ^{13}C NMR SPECTRAL AND PROPERTY STUDIES OF AN INDUSTRIAL BASED SLUDGE LIGNIN

Roger D. McElroy[1] and Ky Lai

Mississippi Forest Products Laboratory
Mississippi State University
Mississippi State, Mississippi 39762

ABSTRACT

A flow scheme was devised for the fractionation-purification of sludge lignin material (mixture of hardwood and softwood) used in the synthesis of a hardboard adhesive. Infrared spectroscopy, proton and carbon-13 nuclear magnetic resonance spectroscopy was used to assign the structure of the sludge lignin. The structural characterization indicated appreciable bond cleavage-rearrangement, and subsequent generation of additional acidic/ketone linkages, p-hydroxyphenyl units and saturated hydrocarbons. Additionally, the sludge lignin based extracts showed good adhesive bonding properties when used in a blend.

INTRODUCTION

In the early twenties, W. H. Mason developed a process for production of hardboard.[2] His process involved preheating of hardwood and softwood chips under steam pressure initially for 40-80 seconds at 150-360 psi in pressure chambers, followed by a rapid increase in pressure to 475-650 psi and a rapid discharge of pressure (gun process) and subsequently blowing the ruptured fiber through a slotted disc. The refined fiber obtained is the raw material used in the hardboard industry. A second process used involved applying steam pressure to the chips in a digester for 2-3 minutes at a pressure of 100-130 psi.[3] The crude sludge material used in this study was ob-

tained as a by-product of the final hardboard production cycle. The crude sludge was found to contain 40-60% lignin and 20-40% carbohydrates.[4] Other materials include wax, cellulose, organic extracts, inorganics and resin.

A great deal of creative research has been published in depolymerization (delignification) extraction and characterization of lignins from wood.[5,6,7] Spectroscopy has been used extensively in molecular structure elucidation of lignins.[8,9,10,11] More recently, solid state ^{13}C NMR spectroscopy has been applied to better characterize insoluble lignins.[12,13]

The objective of this study was threefold: (1) to solubilize the crude sludge material using Kraft hydrolysis or solvolysis,[14] isolate and purify lignin component extracts, (2) to assign the molecular structure of purified lignin via molecular weight, IR, ^{1}H NMR, ^{13}C NMR spectroscopy, chemical composition and functionality, and (3) to evaluate the bonding properties of the lignin extracts when used as a resin.

EXPERIMENTAL

Fractionation-Purification

A 10-15% aqueous-slurry of crude sludge by-product was mixed with 5-10% sodium hydroxide and 1% sodium sulfide in a Parr autoclave and reacted at 100-170^{o}C for 1-2 hours under 75 psi nitrogen pressure. A flow scheme for fractionation-purification of reacted sludge material is shown in Figure 1. Resulting portions were separated into aqueous, acetone soluble fractions. Fractions were evaporated under high vaccum at 40^{o}C over phosphorus pentoxide. The eight fractions were designated: alkali soluble depolymerized sludge material (ASS-1), alkali insoluble sludge (AIS-2), crude lignin (SL-3), acid solubles (AS-4), acetone soluble lignin (SL-5), acetone insoluble lignin (SL-6), acetone soluble-ether insoluble lignin (SL-7), and ether soluble material (ES-8). Yield data is shown in Figure 1.

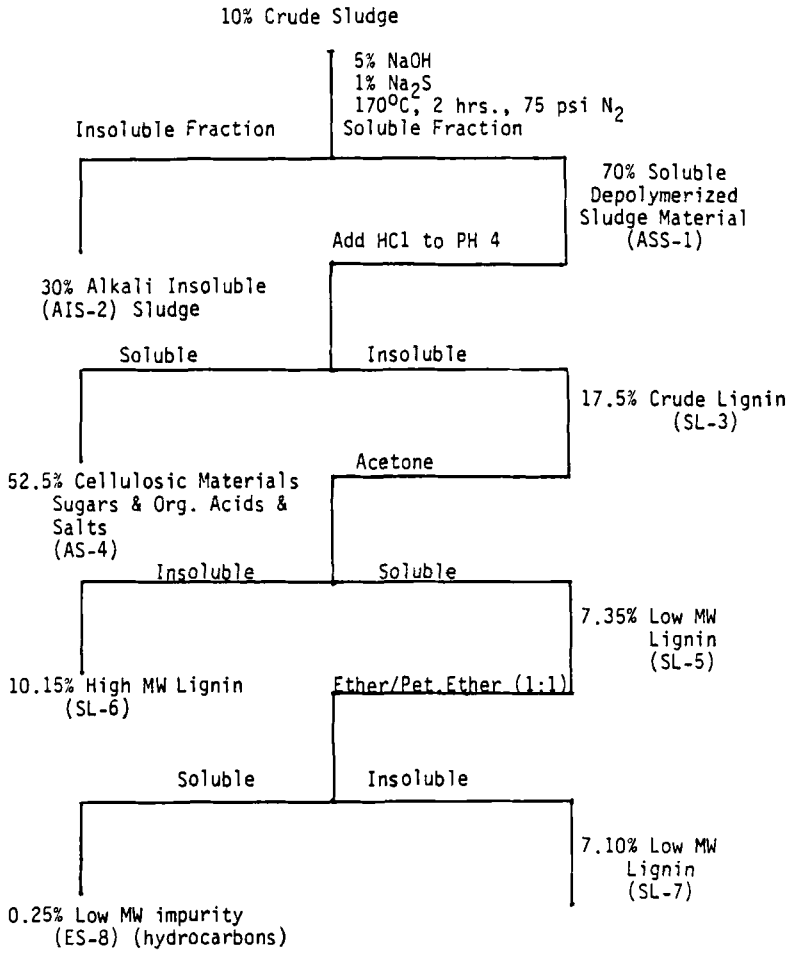

Figure 1. Flow Scheme for Fractionation-Purification of Sludge Lignin.

Solvolysis

A 10% aqueous slurry of the crude sludge by-product was mixed with a 5% sodium hydroxide solution in a Parr autoclave filled to a weight volume of 500 g with dioxane-H_2O(1:1) and reacted at 175°C for one hour under 75 psi nitrogen pressure. The reaction mixture

was filtered and the dioxane evaporated off with a rotary evaporator. The soluble sludge lignin extract was further concentrated and used in the preparation of an adhesive for hardboard.

Spectral Characterization

A Varian CFT-80A nuclear magnetic resonance spectrometer operated at 20 MHz was used to obtain ^{13}C NMR spectra on the acetone soluble sludge lignin fractions (SL-7). A Varian EM-360 nuclear magnetic resonance spectrometer operated at 60 MHz was used to obtain ^{1}H NMR spectra. The ^{1}H NMR and ^{13}C NMR samples were dissolved in dimethylsulfoxide-d_6 solvent and tetramethylsilane was used as the internal standard. Samples analyzed by IR were observed in the form of KBr pellets. The IR spectra was obtained using a Perkin-Elmer Model 283 grating spectrophotometer.

Elemental Analysis

Lignin samples were determined for C, H, O, S, methoxyl content and molecular weight in DMSO solvent using vapor pressure osmometry by Galbraith Laboratories in Knoxville, Tennessee.

Functionality Composition

Total hydroxyl contents were determined by reaction with acetic anhydride in pyridine.[15] Phenolic hydroxyl groups were determined by the use of an ethylated lignin.[16] Total carbonyl was determined by producing the hydrazone with pentaflourophenyl hydrazine.[17] Acidic carboxyl was determined by reaction in a nonaqueous medium with tetrabutylammonium hydroxide.[18]

Resin Preparation

The autoclaved sludge material was either filtered or reacted unfiltered in a weight-volume of approximately 500g. Hexamethylenetetramine (HMTA), epichlorohydrin (epi) or glyoxal (gly) crosslinking reagents were

boiled into the resin mixtures at 100°C for 1 hour. The final sludge lignin adhesive was prepared by blending with commercial phenol-formaldehyde resin (PF-1) or PF resol (low MW) at 100°C or at R. T. for 1 hour.

Similarly, the dioxane-water (1:1) soluble sludge extract portions were first crosslinked, followed by blending with PF-1 resin or PF resol into an adhesive.

The low molecular weight PF resol was prepared by reacting a mixture of 10% sodium hydroxide, 50% phenol and 40% formaldehyde slowly to 60°C, then refluxed for 1 hour, cooled down rapidly and placed in a refrigerator for immediate use.

Property Studies

The sludge lignin-PF resins were applied as a 1% resin by weight. Steam exploded wood was thoroughly mixed with the resin and pressed with a hydraulic press at 150-200 psi for 3 minutes at a temperature of 175°C-200°C. The modulus of rupture (MOR) of hardboards were evaluated using a Tinius-Olsen tensile tester. The boards were subjected to a one hour boil to give the percent swell. These values were compared with a 100 percent commercial phenol-formaldehyde resin (PF-1).

RESULTS AND DISCUSSION

Fractionation-Purification

The sludge material gave a 70% alkali soluble mixture (ASS-1), after being subjected to the Kraft hydrolysis reaction. Figure 1 gives yields of each fraction. The lower molecular weight lignin fraction (SL-7) was obtained in 7.10% yield and the higher molecular weight fraction (SL-6) was obtained in 10.15% yield. Yields are based on total biomass conversion.

Sludge lignin was solubilized in 60%.yield from the solvolysis reaction in dioxane-water (1:1). No further purification was attempted.

Spectral Characterization

This paper will deal primarily with the spectra of the acetone soluble-ether insoluble portion of the sludge lignin (SL-7) and elemental analysis and functionality of both the SL-7 and SL-6 fractions. No usable NMR spectra was obtained for the solvent insoluble lignin fraction (SL-6).

The IR spectra (Fig. 2) give typical hydroxyl stretching absorptions at 2800-3450 cm^{-1}, aromatic bonds at 1510-1600 cm^{-1}, and carbon-oxygen ether bonds at 1000-1400 cm^{-1}. Sludge lignin gave strong broad split signals at 1700, 1735 cm^{-1} which indicate unconjugated ketone and conjugated acid groups. These bonds may be explained as a result of the depolymerization reaction-bond breakage or bond rearrangement leading to increased carbonyl absorptions in the lignin fragment.

The sludge lignin ^{1}H NMR spectra is shown in Figure 3 and the spectra is assigned in Table 1. The assignment of the chemical shifts (Table 1) was made by comparing the spectra range of lignin model compounds.[14,19] The upfield signals at 1.2-1.6 δ were relatively intense due to saturated hydrocarbons. Typical methoxyl (3.8 δ) and aromatic signals (6.5-7.4 δ) were observed.

The ^{13}C NMR spectra of the sludge lignin (SL-7) is shown in Figure 4. The assignment of the peaks in the spectra (Table 2) was made based on comparison of lignin model compounds and natural lignins.[8,9,10,19]

The sludge lignin showed saturated hydrocarbon signals upfield at 10-20 ppm. Additionally, SL-7 gave intense methyl ether absorptions (22.4-24.6 ppm) and both methyl conjugated and unconjugated adjacent ketone signals (28.4-33.7 ppm) respectively. This was confirmed by both the ^{1}H NMR and IR spectra. The SL-7 gave two strong signals at 67.5 pom and 68.5 ppm respectively. These signals may be due to C-γ, C-β in (β-1) dilignol and C-α in (β-O-4) arylglycerol-β-arylether. The

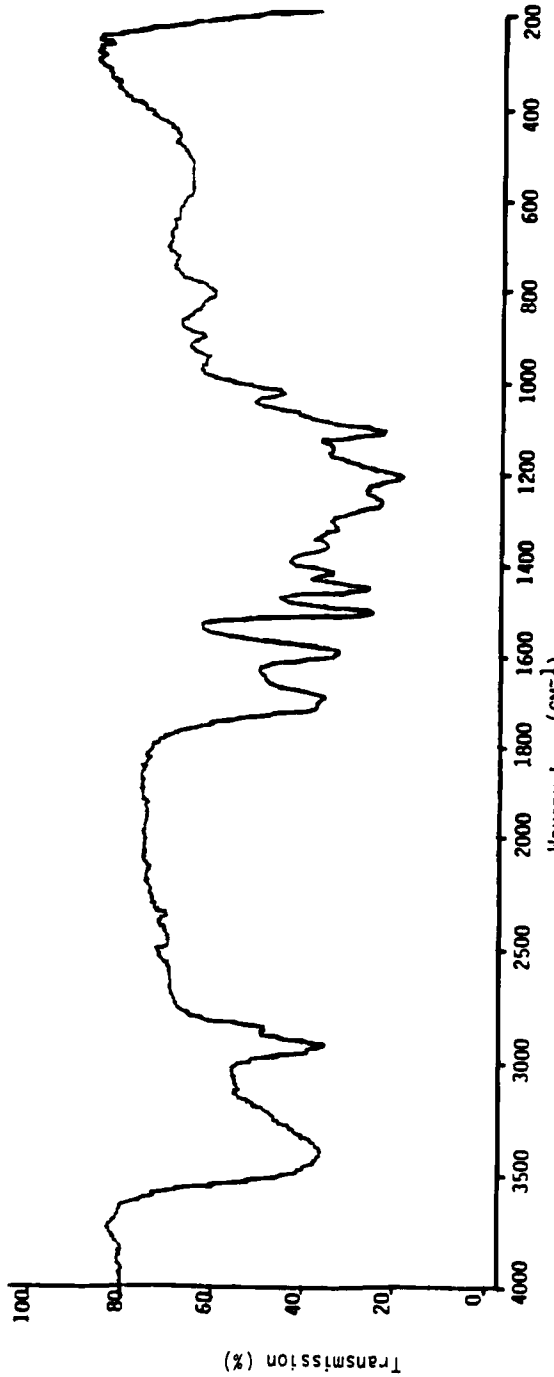

Fig. 2 -- IR Spectra of Sludge Lignin (SL-7) in KBr pellet.

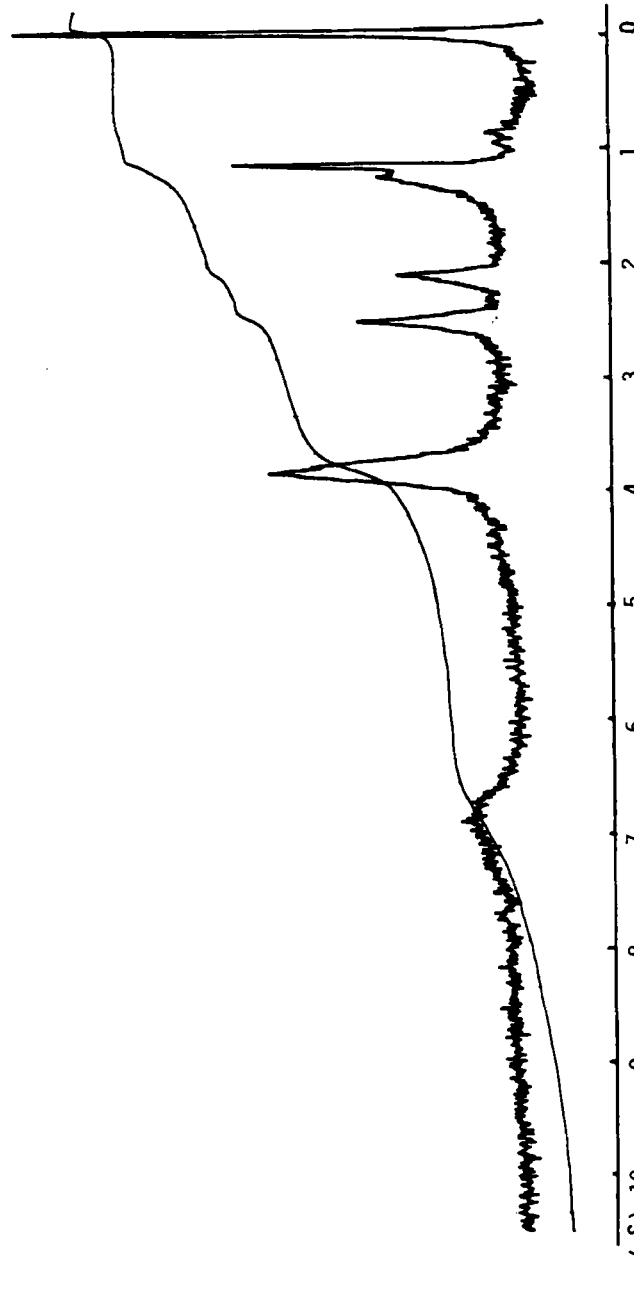

Fig. 3 -- ^{1}H NMR Spectra of Sludge Lignin (SL-7) in DMSO-d_6.

TABLE 1

Assignment of ^{1}H NMR Spectra of Sludge Lignin (SL-7). Chemical Shifts are Given in δ Values Downfield from TMS in DMSO-d_6 Solvent.

ppm(δ)	Intensity	Assignments
1.2-1.3	S	Highly shielded methyl, methylene or methinyl aliphatic hydrocarbons.
2.1-2.2	M	Methyl or methylene protons adjacent to ketone group or double bond.
2.5	M	Aliphatic methoxyl protons.
3.8	S	Aromatic methoxyl protons.
4.2-4.5	VW	H-C γ in (β -O-4) arylglycerol-β-arylether.
5.0-5.2	VW	H-C γ in cinnamyl, H-C β in (β -O-4).
5.4-5.7	VW	H-C α in (β -5) phenylcoumaran.
6.4-7.4	M	Aromatic protons.
7.7-7.9	W	p-Hydroxyphenyl aromatic protons.

sludge lignin gave strong signals at 115.7 ppm, 128.7 ppm and 131.5 ppm characteristic of hydroxyphenyl units.

The SL-7 lignin gave a strong absorption of 147.9 ppm which can be attributed to both guaiacyl and syringyl units evident in both hardwood and softwood. In the range (165.4-172.0 ppm) α, β, γ carboxylic acid carbonyls are present in the sludge lignin as was confirmed by ^{1}H NMR and IR. Additionally, the SL-7 showed a weak carbonyl absorption (206.0 ppm) for unconjugated ketones which again was shown in the IR spectra.

Chemical Analysis and Functionality

Elemental analysis and molecular weight (Table 3) would tend to indicate the following trends: (1) higher C content in the SL-7 portion may be due to condensation reactions and hydrocarbon residues, (2) lower OCH_3 and corresponding higher total OH functionality in the SL-6 fraction may arise through increased demethoxylation with subsequent formation of free phenolic groups and hence greater solvent insolubility, (4) the greater sulfur content shown in the SL-7 fraction may be due to the increase in the number of mercaptans, sulfonic acids or sulfhydryl linkages formed through Kraft hy-

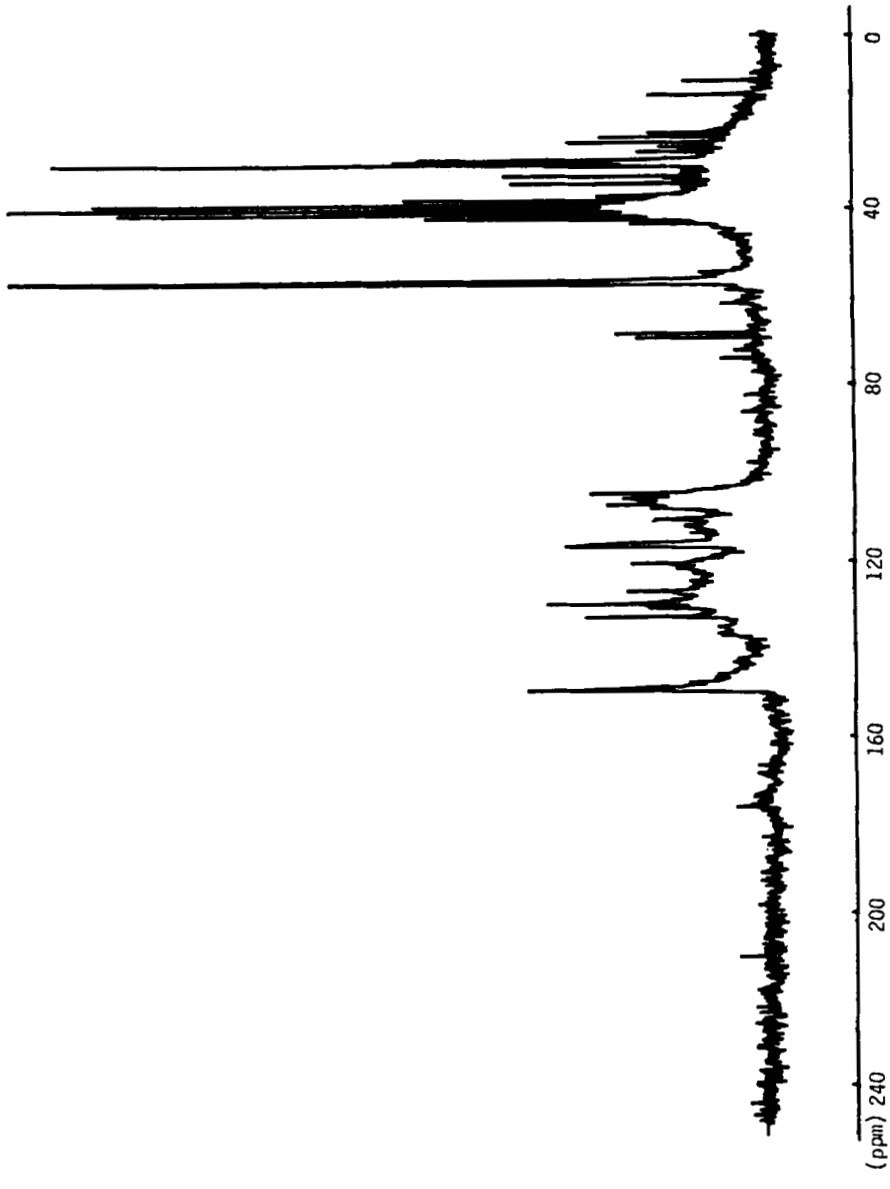

Fig. 4 -- ^{13}C NMR Spectra of Sludge Lignin (SL-7) in DMSO-d_6.

TABLE 2

Assignment of ^{13}C NMR Spectra of Sludge Lignin (SL-7), as Shown in Figure 4.

Chemical Shifts in PPM

PPM	Intensity	Assignments
10.0-13.9	M	Saturated hydrocarbons
22.4-24.6	M	Methyl in aliphatic ethers
28.4-33.7	S	Methyl in Ketones (conj.)
39.6	VS	DMSO-d_6
55.8	VS	Methoxy in quaiacyl
67.5	S	C-γ, C-β in (β-1) dilignol
68.5	S	C-α in (β-O-4) arylglycerol-β-arylether
70.7-73.2	W	C-γ in syringylaresinol and (β-β) dibenzyltetrahydrofuran
81.5	VW	C-β in α-carbonyl-β-arlether
85.2	VW	C-α in pinoresinol
103.9-104.9	M	C-2,C-6 in syringyl
106.4-107.2	W	C-2,C-6 in syringyl (with α-C=O, α-HC-C)
109.8-112.0	W	C-2 in guaiacyl ether
115.7	S	C-5 in guaiacyl, C-3,C-5 in p-hydroxylphenyl
119.6	M	C-6 in guaiacyl
125.8	M	C-6 in guaiacyl, C-β in coniferyl
128.7-129.7	M	C-2,C-6 in p-hydroxyphenyl
131.5	S	C-β in cinnamaldehyde, C-1^1 in (β-1) dilignol
134.8	W	C-1 in guaiacyl ether
141.4	VW	C-1,C-4 in syringyl ether
147.6	M	C-4 in guaiacyl
147.9-148.0	M	C-3 in guaiacyl, C-3,C-5 in syringyl
165.4-172.0	VW	α, β, γ carboxyl in acids or ketones
206.0	W	Carbonyl in ketones (unconj.)

Intensity abbreviations used: S=strong, M=medium, W=weak, VS=very strong, VW=very weak

TABLE 3. Chemical Analysis and Functional Group Composition

Lignin Fraction	C%	H%	O%	S%	OCH_3%	Total OH	Phenolic OH	Total Carbonyl	Total Carboxyl	MW
SL-6	58.24	5.19	34.09	2.48	8.51	14.50				
SL-7	63.64	6.10	25.20	5.06	14.07	11.29	5.20	1.85	1.10	550

TABLE 4

Yield of Solubilized Sludge Lignin
After Various Pretreatments

Run No.	Crude Sludge (%)	NaOH (%)	Na_2S (%)	Reaction Conditions (°C)	Solubilized Sludge (%) Pretreated	No Pretreated
1	15	10	1	100°, 1 hr.	40.0[a]	43.0
2	15	10	1	100°, 1 hr.	42.9[b]	43.0
3	15	10	2	100°, 1 hr.	36.0[a]	32.2
4	15	7	2	100°, 1 hr.	38.2[b]	38.5
5	15	5	1	100°, 1 hr.	39.7[b]	40.0
6	10	5	1	170°, 2 hr.	70.0[c]	--
7	15	10	0	100°, 1 hr.	30.1[b]	31.3
8	15	10	5	100°, 1 hr.	42.5[b]	44.1
9	10	5	1	170°, 1 hr.	67.0[c]	--
10	10	5	0	175°, 1 hr.	60.0[c,d]	--

[a]Boiled with 1% sulfuric acid to remove residual carbohydrates.

[b]Boiled with 1% sulfuric acid and washed with acetone to remove carbohydrates, waxes and extractives.

[c]Washed with acetone, MeOH and hexane to remove the waxes and extractives.

[d]Solvolysis: dioxane/water (1:1).

drolysis, and (5) the low MW SL-7 fraction may be the result of monomeric, dimeric or trimeric fragmented units, particularly evident when the lignin is subjected to vigorous reaction conditions.

Property Studies

As evident from Table 4, reaction 6, the sludge material was solubilized almost twofold at 170°C using 10% sludge starting material versus

TABLE 5

Hardboard Properties Using Filtered Sludge Lignin/PF Resins
Lignin Extract via Dioxane-Water (1:1) Solvolysis

Resin No.	Autoclave Reaction T(^{o}C) time (hr.)	Formulation	Parts by Weight	MOR psi (No. of Boards)	1-hr Boil Swell, %
1	175^{o} 1 hr.	Soluble sludge lignin NaOH HMTA PF resol	1.0 0.50 0.067 1.0	5361 (8)	48
2	175^{o} 1 hr.	Soluble sludge lignin NaOH HMTA PF-1	1.0 0.50 0.067 1.0	5394 (3)	50
3	175^{o} 1 hr.	Soluble sludge lignin epi PF resol NaOH	1.0 0.16 1.0 0.50	4907 (8)	92
4	175^{o} 1 hr.	Commercial lignin HMTA PF resol NaOH	1.0 0.067 1.0 0.50	4788 (2)	61
5	175^{o} 1 hr.	Soluble sludge lignin gly PF resol NaOH	1.0 0.16 1.0 0.50	5161 (8)	75
6		PF-1		5276 (5)	62

100^{o}C. Greater sodium hydroxide and sodium sulfide concentrations tended to increase the soluble yields as shown in runs No. 1, 2, and 8.

The desired physical properties of the hardboard resins were: MOR=5000+; and 1 hour boil swell percent of 50±10. Therefore, HMTA crosslinked soluble sludge lignin (Table 5) obtained by solvolysis in dioxane-water (1:1) gave favorable MOR and boil swell values when compared with a control PF-1 resin. This resulted in a 50 percent replacement for the PF resin used in the hardboard process.

TABLE 6

Hardboard Properties Using Filtered Soluble Sludge Lignin/PF Resins in Aqueous Alkali Systems

No.	Autoclave Reaction T (^{o}C) time (hr.)	Formulation	Parts by Weight	MOR psi (No. of Boards)	1-hr Boil Swell,%
1	170^{o} 2hrs.	Soluble sludge lignin	1.0	4944 (4)	58
		NaOH	0.50		
		Na_2S	0.10		
		HMTA	0.033		
		PF-1	1.0		
2	170^{o} 1hr.	Soluble sludge lignin	1.0	5414 (3)	57
		NaOH	0.67		
		Na_2S	0.067		
		HMTA	0.033		
		PF-1	1.0		
3	170^{o} 1hr.	Soluble sludge lignin	1.0	5444 (4)	62
		NaOH	0.33		
		Na_2S	0.067		
		HMTA	0.033		
		PF-1 (R.T.)	1.0		
4	170^{o} 1hr.	Ins. recycled sludge	1.0	3332 (4)	86
		NaOH	0.33		
		Na_2S	0.067		
		HMTA	0.033		
		PF-1	1.0		
5	100^{o} 1hr.	Soluble sludge lignin	1.00	5101 (4)	48
		NaOH	0.33		
		Na_2S	0.067		
		HMTA	0.033		
		PF resol	1.00		
6	170^{o} 1hr.	Soluble sludge lignin	1.00	5309 (4)	54
		NaOH	0.33		
		Na_2S	0.00		
		HMTA	0.033		
		PF-1	1.00		

TABLE 6
continued

7	100° 1 hr.	Soluble sludge lignin NaOH Na_2S HMTA PF resol	1.0 0.50 0.00 0.00 1.0	5180 (2)	72
8	100° 1 hr.	Soluble sludge lignin NaOH Na_2S CH_2O PHOH	1.0 0.60 0.20 0.70 1.0	5170 (2)	65
9	170° 2 hrs.	Soluble sludge lignin NaOH Na_2S HMTA PF resol	1.0 0.50 0.00 0.067 1.0	5207 (3)	45
10	100° 1 hr.	Soluble sludge lignin NaOH Na_2S HMTA PF-1	2.00 0.50 0.067 0.033 1.0	3402 (2)	58
11	100° 1 hr.	Soluble sludge lignin NaOH Na_2S HMTA PF-1	1.00 0.33 0.067 .033 0.00	3085 (2)	85
12	170° 1 hr.	Unfiltered sludge lignin NaOH Na_2S HMTA PF resol	1.00 0.50 0.10 0.00 1.00	5200 (5)	56
13	100° 1 hr.	Unfiltered sludge lignin NaOH Na_2S HMTA PF-1	1.00 0.33 0.067 0.033 1.00	4819 (10)	36
14		PF-1		5438 (4)	52

Table 6 shows the hardboard properties of soluble sludge lignin / PF and two unfiltered sludge mixtures / PF resins, No. 12-13. These results indicate that the sludge material autoclaved in alkali medium at either 170°C or 100°C will give good bonding properties. The higher temperatures increased the solubility of the material. Additionally, the unfiltered sludge material, after autohydrolysis, met the criteria for the hardboard resin. However, when the amount of sludge lignin extract was increased by twofold, run No. 10, the MOR fell well below the specifications. Also, when the PF-1 or PF resol was not cooked into the resin mixture, the bonding properties of the resin gave poor results. An attempt was made to autoclave a second time the soluble sludge (No. 4) that was filtered off from the first hydrolysis. This recycled sludge gave both unsatisfactory MOR and boil swell values. An autoclave load of 10-15% crude sludge, 5-10% sodium hydroxide, and 0-1% sodium sulfide gave good properties. The HMTA served as a successful catalytic crosslinking reagent. The good bonding properties of the unfiltered sludge mixtures may have been due in part to the carbohydrate components present in the crude slurry. From the data obtained, the sludge by-product can be successfully converted into a usable resin at a 50 percent substitution rate for the phenol-formaldehyde systems.

Conclusions

The spectroscopy, chemical analysis and functionality studies of the sludge lignin led to the conclusion that the sludge material (initially steam exploded followed by Kraft hydrolysis) resulted in appreciable bond cleavage-rearrangement, and subsequent generation of additional acidic/ ketone linkages, p-hydroxyphenyl units and saturated hydrocarbons.

A commercially viable alternative adhesive system was successfully developed for the hardboard industry through the biomass conversion, molecular structural characterization, resin synthesis and property studies of an otherwise useless sludge waste material.

Acknowledgements

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