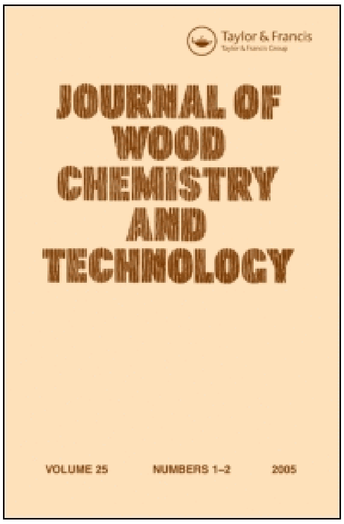

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Electrochemistry of Biomass-Derived Materials I. Characterization, Practionation, and Reductive Electrolysis of Ethanol-Extracted Explosively-Depressurized Aspen Lignin

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ELECTROCHEMISTRY OF BIOMASS-DERIVED MATERIALS
I. CHARACTERIZATION, FRACTIONATION, AND REDUCTIVE ELECTROLYSIS OF ETHANOL-EXTRACTED EXPLOSIVELY-DEPRESSURIZED ASPEN LIGNIN

By

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ABSTRACT

The chemical characterization (functional group distribution) and spectroscopic properties (^{13}C, ^{1}H, IR, UV-Vis) of a number of lignins obtained from ethanol extraction of explosively-decompressed aspen (*Populus tremuloides*) lignin (EEEDAL) are described. In this process wood is heated to ~240°C by direct steam and fiberized by sudden decompression. Both mechanical and chemical degradation occur which lead to a decrease of the molecular weight of all of the natural polymers. The lignin fraction is soluble in alcohols; it has a low number average molecular weight (925) and is very reactive. EEEDAL was subjected to fractionation by differential solubility prior to and after electrolyses on mercury cathodes at -2.6 V vs. Ag/AgCl in methanol/tetraethylammonium perchlorate. After recovery of 85-90% of the original weight of material used by precipitation with acid, followed by a series of extractions, the chemical and spectroscopic properties of each fraction were determined. The acid-insoluble fractions are more condensed than the acid-soluble fractions and have lower phenolic OH and lower aliphatic OH contents than the acid-soluble fractions. The acid-soluble fractions phenolic OH content approaches one per phenylpropane (C_9) unit of the lignin. Electrolyses increase the amount of lower molecular weight, high phenolic content, acid-soluble lignins and changes the molecular weight distribution by decreasing the polydispersity of the resulting lignins. These low-molecular-weight lignins are chemically reactive (for instance, with formaldehyde) and can be used in the partial replacement of phenol in phenol-formaldehyde thermosetting resins.

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INTRODUCTION

Lignins[1] are complex, cross-linked phenyl propane polymers which compose, together with cellulose and other carbohydrates, the cell wall structural members of living plants. A crucial step in the biosynthesis of lignins is the enzyme initiated dehydrogenative coupling of three substituted cinnamyl alcohols, viz. 4-hydroxy-3-methoxycinnamyl (coniferyl) alcohol, 4-hydroxy-3,5-dimethoxycinnamyl (sinapyl) alcohol and 4-hydroxycinnamyl (p-coumaryl) alcohol. The proportion of each alcohol in the polymer is a function of the species. For instance, in hardwoods such as aspen (*Populus tremuloides*) the lignin is derived predominantly from coniferyl and sinapyl alcohols.

Many lignin structural investigations deal with milled wood lignins, kraft lignins, and lignosulfonates but as yet only a few studies have concentrated on lignins isolated from steam exploded (explosively decompressed) wood and new pretreatments of wood[2a,b] Marchessault *et al.*[2c] have investigated the variation of the properties of aspen lignin, isolated after explosive depressurization, as a function of the explosion temperature and a comparative study by Glasser *et al.*[2d] of a large number of different lignin preparations included a brief examination of sodium hydroxide extracted steam exploded lignins. Hemmingson[2e] described the effect of steam explosion on the softwood *Pinus radiata* lignin. A recent symposium on wood and pulping chemistry contains papers on characterization of some explosively depressurized aspen[2f] and beech[2g] lignins.

The present paper describes the chemical and spectroscopic characterization of ethanol-extracted aspen wood which has undergone explosive depressurization. In this process the wood is heated to ~240°C by direct steam and is fiberized by sudden decompression. Both mechanical and chemical degradation occur which renders the hemicellulosic part of the wood almost completely hot water soluble. About 90% of the lignin, which has a relatively low molecular weight, can be solubilized readily in ethanol/water

(90% v/v), while the cellulose, although having a decreased degree of polymerization, remains largely crystalline and therefore insoluble. Subsequent fractionation of the lignin by precipitation with acid from an alkaline methanol solution yielded lignin samples with different physical and spectroscopic properties.

Electrochemical reactions of lignin preparations have been carried out only to a very limited extent and have formed the subject of a recent review.[3] A number of polarographic studies of lignins have been reported[4] and in all cases the polarograms indicated irreversible electron transfer, often associated with adsorption of the lignin on the dropping mercury electrode (DME). Up to four reduction waves have been observed for lignin in non-aqueous solvents.[5] The preparative scale reduction of dioxane lignin and kraft lignin in aqueous ammonia solutions by electrochemically generated ammonium amalgam led to low molecular weight monomeric and dimeric products.[6] Most of the electrolyses of lignin preparations reported, however, utilize ill-characterized lignins and were not followed by full product characterization.

We have carried out electrochemical reductions of our well characterized ethanol-extracted explosively-depressurized aspen lignin (EEEDAL) at mercury cathodes in methanol/tetraethylammonium perchlorate. After recovery of 85-90% of the original weight of material used by precipitation with acid, followed by a series of extractions, the chemical, physical, and spectroscopic properties of each fraction were determined.

EXPERIMENTAL

Materials

Ethanol-Extracted Explosively-Decompressed Aspen Lignin (EEEDAL): The lignin was isolated from explosively decompressed aspen wood (supplied by Iotech Corp.) (55 seconds residence time at 240° C) by a procedure similar to that described by Marchessault and St. Pierre.[7] Explosively decompressed aspen wood (602 g, moisture content on an ovendried basis, 60%) was stirred vigorously with water (5.25 dm^3) at room temperature for 3 hours to remove the soluble hemicelluloses. The insoluble lignocellulosic fraction was filtered and washed with water (10 dm^3) and then added to ethanol (5.25 dm^3). After stirring vigorously at room temperature, under nitrogen, overnight, the mixture was filtered and the insoluble cellulosic material was washed with ethanol (2 dm^3). The filtrate and washings were combined and the ethanol evaporated under reduced pressure. A dark brown glassy solid (43 g, 78% yield based on Klason lignin in dry wood) was obtained after drying under vacuum.

The EEEDAL thus prepared contains two types of impurities: a) 1.0 wt % water-soluble monosaccharides, determined according to reference 8; b) 5 wt % of carbon tetrachloride-soluble organic compounds; these impurities are probably derived from the extractives fraction of aspen, which contains primarily fatty acids.[9] Both the IR and NMR spectra of the CCl_4 extracts are compatible with mixtures of fatty acids and fatty alcohols. Electrolyses were carried out with the EEEDAL containing extractives impurities. Spectral and analytical data were obtained of samples with and without extractives.

Other materials: Methanol was used as supplied by Mallinkrodt for preparative electrolyses. Tetraethylammonium perchlorate was used as supplied by G. F. Smith. The triply distilled mercury (Bethlehem) was used without further purification. All other solvents and chemicals utilized were reagent grade.

ELECTROCHEMICAL CELLS AND INSTRUMENTATION

For controlled potential electrolyses one of two potentiostats was used; either a Bioanalytical Systems SP2 or a Wenking HP72. To measure the charge consumed a digital coulometer was employed (ESC 640). All lignin reductions were carried out in a glass cell with a stirred mercury pool cathode (area ≈ 16 cm^2 or 38 cm^2). The secondary electrode (platinum disc; area ≈ 12 cm^2) was parallel to the working electrode and separated from the catholyte by a sintered glass disk.

LIGNIN ELECTROLYSIS AND FRACTIONATION PROCEDURE

About 150 cm^3 of deaerated 0.1 mol dm^{-3} Et_4NClO_4 in methanol were placed in the cathode compartment of the cell and preelectrolyzed (at −2.6 V *vs*. Ag/AgCl) until a constant low current value was obtained prior to the addition of the lignin (3.0 g, ~3 × 10^{-3} mol). The lignin was then reduced at −2.6 V (*vs*. Ag/AgCl) until the current reached that of the background. Towards the end of the electrolysis the color of the catholyte, originally dark brown, became yellow. Throughout the electrolysis, except during the initial 5 minutes, the pH of the solution was 12.0. To isolate the products the reduced lignin solution was siphoned out of the cell to below the surface of cold, deoxygenated hydrochloric acid (300 cm^3, 0.5 mol dm^{-3} at *ca*. 2° C). The precipitated lignin, the acid insoluble fraction (AI) (a light brown or beige finely divided solid), was separated by centrifugation (10,000 rpm, 30 minutes). The supernatant liquid was retained and the solid material was resuspended in water (500 cm^3). After centrifugation the washing process was repeated once again followed by drying in a vacuum desiccator (over P_2O_5 or H_2SO_4) to give a light brown solid (1.6-1.8 g). To isolate the lignin remaining in the supernatant liquid, the solution was saturated with potassium chloride and extracted with ethyl acetate (3 × 100 cm^3). The combined extracts were washed (saturated sodium chloride solution, 50 cm^3), dried ($MgSO_4$) and the solvent evaporated under reduced pressure. Final drying in a vacuum desiccator gave a brown glassy material (0.5-0.9 g), the acid-soluble fraction (AS). The samples were kept under vacuum until they were analyzed. The removal of the lignin still dissolved in the aqueous layer, the very soluble fraction (VS), was accomplished by evaporating the solution to a low volume (under reduced pressure) and then adding methanol (100

cm^3). After stirring to solubilize the lignin, the solution was filtered and the salts remaining were washed with a further portion of methanol (50 cm^3). The combined methanol solutions were evaporated under reduced pressure until the volume was ca. 30 cm^3. When the solution had cooled to room temperature it was transferred to a volumetric flask (50 cm^3) and was made up to volume with water and methanol. The lignin solution was then analyzed for carbonyl group content by using a modification of the procedure reported below.

Exploratory lignin electrolyses at other potentials were also carried out. Since the objective of the work was to carry out exhaustive reductive electrolysis and affect the largest extent of reductions (without using solvated electrons), the analytical results were mainly devoted to electrolyses carried out at -2.6 V vs. Ag/AgCl. Constant current electrolysis could have been employed.

FRACTIONATION OR "BLANK ELECTROLYSIS" PROCEDURE

Lignin (3.0 g, ~3 × 10^{-3} mol) was dissolved in methanol/Et_4NClO_4 (0.1 mol dm^{-3}, 150 cm^3) and the pH was adjusted to 12 by adding sodium methoxide. After stirring at room temperature under nitrogen for 3 hours, the lignin was isolated by the same procedure as that described above.

Table 1 summarizes the results of the fractionation procedure as well as the electrolysis and fractionation on EEEDAL.

Acetylation Procedure: A method similar to that employed by Gierer and Lindeberg[10] was used. The reactions were carried out at 40°C overnight. Toluene impurities were removed by azeotropic ethanol evaporation.

ANALYTICAL METHODS

The analytical data on the lignins investigated in this paper are assembled in Table 2.

Table 1. Definition of the conditions used in the isolation of the lignins and yields. EEEDAL = ethanol-extracted explosively-depressurized aspen lignin, F = fractionation; A = acid; S = soluble; I = insoluble; V = very; E = electrolysis

Experiment	Sample Description	% Recovery (includes extractives)
No electrolysis	EEEDAL	--
Fractionation at pH = 12 (Blank electrolysis)	FAI-12[a]	67
	FAS-12[b]	25
	FVS-12[c]	8
Electrochemical reduction 3 g EEEDAL/CH_3OH + Et_4NClO_4 (0.1 M) -2.6 V vs Ag/AgCl; 2900 coulombs	EFAI-12[d]	54
	EFAS-12[e]	30
	EFVS-12[f]	15
Fractionation at pH = 7 (Blank electrolysis)	FAI-7[g]	73
	FAS-7[h]	14
	FVS-7[i]	13

[a] Material precipitated when EEEDAL (3 g/150 cm^3 CH_3OH, 0.1 M Et_4NClO_4) at pH = 12 (by addition of $NaOCH_3$) for 2-3 hours, was added to 500 cm^3 of 0.5 M aqueous HCl.

[b] Material obtained by extraction in ethyl acetate of the NaCl saturated supernatant of a.

[c] Residue soluble in b and not extractable in ethyl acetate.

[d-f] Materials prepared under analogous conditions to a-c, respectively, but with electrolysis of EEEDAL.

[g-i] Materials prepared under analogous conditions to a-c, respectively. but at pH = 7.0.

Elemental Analyses: Performed by Huffman Laboratories, Denver, Colorado.

Methoxy Content: The standard procedure[11] was employed. In many cases, since the samples were small (<20 mg), a larger analytical error was observed (15%). A second procedure used was quantitative[12] ^{13}C NMR (see Spectral Analyses, NMR) while a third procedure used IR (see spectral analyses, IR).

Table 2. Analytical composition, C_9 formulas of EEEDAL and lignin samples described in Table 1.

		Elemental Analysis % wt		Functional Group Analysis, % wt			C_9 Formula
		C	H	OH	OCH_3	C=O	
EEEDAL	Chemical Analysis (CA)	64.84[a] 63.6[b]	6.28[a] 6.06[b]	10.5	18.2	2.8	$C_{9.0}H_{7.0}O_{1.1}(O_{CO})_{.2}(OH)_{1.2}(OCH_3)_{1.1}$
Acetylated EEEDAL	CA and ^{13}C NMR	65.11	5.91	--	15.8	--	$C_{9.0}H_{5.9}O_{1.0}(O\underset{O}{C}CH_3)_{1.15}(OCH_3)_{1.2}$
FAS-12	CA and ^{13}C NMR	59.57	5.70	10.4	18.5	3.0	$C_{9.0}H_{6.7}O_{1.8}(O_{CO})_{.2}(OH)_{1.3}(OCH_3)_{1.2}$
EFAS-12	CA	62.16	6.45	13.2	18.7	0.8	$C_{9.0}H_{7.6}O_{1.2}(O_{CO})_{.06}(OH)_{1.4}(OCH_3)_{1.2}$
FAI-12	CA and ^{13}C NMR	66.02[a] 65.1	6.40[a] 5.9	10.1	17.5	2.5	$C_{9.0}H_{6.6}O_{1.0}(O_{CO})_{.2}(OH)_{1.1}(OCH_3)_{1.05}$
EFAI-12	CA	67.18[a] 66.4[c]	7.02[a] 6.63[c]	10.5	17.8	0.55	$C_{9.0}H_{7.7}O_{.9}(O_{CO})_{.04}(OH)_{1.1}(OCH_3)_{1.05}$
FAS-7	CA	61.39	5.79		18.1	3.8	$C_{9.0}H_{8.0}O_{2.6}(O_{CO})_{.3}\quad(OCH_3)_{1.15}$
FAI-7	CA	65.38 64.8[b]	6.31 6.0[b]	10.3	18.5	2.4	$C_{9.0}H_{6.0}O_{1.1}(O_{CO})_{.2}(OH)_{1.15}(OCH_3)_{1.15}$

[a] Elemental analysis of lignin in the presence of ~5% extractives impurities.

[b] Elemental analysis calculated discounting ~5% extractives impurities.

[c] Approximate elemental analysis discounting ~7.5% extractives impurities.

Carbonyl content: The oximation of the carbonyl groups was used following the procedure of Gierer and Lenz.[13] The pH (Orion 91-02 combination electrode) was kept constant at 4.0 with the automatic titration system (Methrohm E526 Titrator with Methrohm 655 Dosimat motorized burette). The reaction was carried out at 35° C (MGW Lauda T1 thermostat circulator) for about 24 hours. The accuracy of the method was tested with several lignin model compounds containing α-carbonyl groups. The reproducibility of the method is ±4%.

Phenolic Hydroxy Content: The procedure of Sarkanen and Schuerch[14] was utilized, with the Methrohm E518 conductimeter, and conductivity cell OH 9100. The reproducibility of the method is ±4%. A second procedure used the ^{13}C NMR spectra of the acetylated materials[12] and as a third procedure, the UV difference spectrum between pH 14 and pH 5 was used.[15]

Total Hydroxy Content: The lignin samples were methylated three times with dimethylsulfate according to a modification of the procedure in reference 16. The analytical methoxy determination was repeated on the methylated lignin. The calculation of the total hydroxy content follows the method of Browning.[17] Alternatively, quantitative ^{13}C NMR was used to determine the total hydroxy content, as well as the proportion of aliphatic and phenolic OH groups present.

Catechol Content: Ca. 1.3% w/w of catechol groups were found in EEEDAL following a colorimetric procedure.[18]

Carboxylic Acid Content and Evaluation of Impurities: After stirring for 15 minutes a sodium bicarbonate solution containing finely ground lignin (0.5 g), the unreacted sodium bicarbonate is titrated with HCl using a pH electrode (Orion 91-02) and meter (Orion 701 A). Difference of the end-point of this titration with that of a sample of the sodium bicarbonate solution employed, yields the carboxylic acid content. The method was originally tested with salicylic acid to test the possibility of interference of phenolic groups. The results were accurate to ±1%.

The lignin isolated by extracting the explosively-depressurized aspen wood with dilute NaOH had a carboxylic acid content of ca. 0.8% by weight. All of the acid soluble fractions had a very small carboxylic acid content. A content of carboxylic acid of ~0.5% by weight corresponds to an error in the phenolic hydroxy analysis of 0.2%.

p-Hydroxybenzoic esters are known to be a major component of the milled wood aspen lignin (up to 10% w/w have been detected in some cases).[1a] During the explosive depressurization, some of the ester units might have hydrolyzed. We attempted to determine the content of p-hydroxybenzoic acid from the wood after explosion, as well as to hydrolyze the EEEDAL under alkaline conditions to ascertain how much of the ester can be converted into the p-hydroxybenzoic acid. In 75 cm^3 of water, 8.4 g of wood were suspended and stirred for 5 hours. After filtration, the yellow solution was evaporated under reduced pressure to yield a red brown oil. The oil was stirred with saturated $NaHCO_3$ solution and filtered off and washed with $NaHCO_3$. The solution was made acidic with concentrated HCl and extracted with 4 × 30 cm^3 of ether. The combined ether extracts were water washed, dried with $MgSO_4$ and evaporated to dryness. The yield was 22 mg of which thin-layer chromatography, IR and UV absorption spectra identified as containing p-hydroxybenzoic acid (~25% by UV-absorption spectroscopy). This yield indicates that about 1% w/w (with a relatively large error due to the many extractions) of the lignin was extracted as p-hydroxybenzoic acid.

This material is not present in the EEEDAL because of the water extraction procedure employed to remove the soluble hemicellulosic fraction also solubilizes the p-hydroxybenzoic acid.

A similar extraction procedure was employed with EEEDAL except that sodium hydroxide (2M) was employed. From 1 g of EEEDAL, 24 mg of a yellow oil was obtained, which contained ~15% of p-hydroxybenzoic acid. In other words, ~0.5% w/w of p-hydroxybenzoic acid could be isolated from EEEDAL after hydrolysis. That amount would correspond to ~0.15% of carboxylic acid groups. In the titration procedure employed for carboxylic acid determination, this whole content of carboxylic acids would not be hydrolyzed during the titration time. Therefore, the major fraction of carboxylic acids measured by the titration procedure employed above can be attributable to fatty acid impurities. Albeit the error of determinations of p-hydroxybenzoic acid is large, the steam exploded aspen utilized in these studies does not seem to contain but 2-3% w/w of p-hydroxybenzoic acid.

Assuming that all of the carboxylic acid content is due to fatty acid impurities implies that ~5% by weight of the EEEDAL is fatty acids (the average molecular weight of the fatty acids in aspen was considered ~320; the elemental analysis of the carbon tetrachloride extracted fraction is: 77.9% C; 11.4% H; 10.7% O). Based on this number, on the yield of the CCl_4 extract, and on the carbohydrate impurities, we estimate the total impurity content of EEEDAL as ~5% by weight.

SPECTRAL ANALYSES

Infrared absorption spectra of the lignins were recorded by a Perkin Elmer 599B spectrophotometer. Pellets of 1 mg lignin/300 mg KBr were used. The evaluation of the band intensities was carried out using the method of Sarkanen, Chang, and Allan.[19] Table 3 assembles the percent of guaiacyl groups and the ratio of OCH_3/C_9 based on the percent absorptivities of characteristic spectral maxima (1600, 1460, 1325, 1230, and 1120 cm^{-1}) relative to that at 1500 cm^{-1}, assigned to aromatic skeletal vibrations.

Ultraviolet and visible absorption spectra of ethanolic lignin solutions were recorded by a Hewlett-Packard 8450A spectrophotometer. Difference spectra were recorded in aqueous media.

A FT-NMR spectrometer JEOL FX-90Q was employed for obtaining spectra of acetylated lignins (60-75 mg/.4 ml $CDCl_3$) with ~1% TMS as internal standard. For proton spectra, single pulses (15 μs) were employed with a pulse interval of 4.55 s and an accumulation

Table 3. **Evaluation of the OCH_3/C_9 ratio and the guaiacyl content of EEEDAL and lignin samples described in Table 1 by infrared spectroscopy.**[a,b]

Sample	i=1460 cm^{-1}			i=1325 cm^{-1}			i=1220 cm^{-1}			%G[c]	$\frac{OCH_3}{C_9}$ [c]
	A_{1460}/A_{1500}	%G	OCH_3/C_9	A_i/A_{1500}	%G	OCH_3/C_9	A_i/A_{1500}	%G	OCH_3/C_9	Average	Average
EEEDAL	.70± .05	73	1.27± .07	.49± .03	62±3	1.38± .06	.83± .04	82±4	1.18± .06	74±9	1.26± .09
EEEDAL[d]	.63	78	1.22	.48	63	1.37	.80	84	1.16	76±9	1.24± .08
FAS-12	.65	77	1.23	.49	62	1.38	.89	76	1.24	67±9	1.33± .09
EFAS-12	.69	74	1.26	.39	70	1.30	.84	80	1.20	72±6	1.28± .06
FAI-12	.64	77.5	1.22	.42	67	1.33	.82	83	1.17	77±7	1.23± .07
EFAI-12	.69	74	1.26	.41	68	1.32	.85	79	1.21	77±6	1.23± .06
FAS-7	.67	75	1.25	.51	61	1.39	.75	89	1.11	73±10	1.27± .1
FAI-7	.65	77	1.23	.39	70	1.30	.83	82	1.18	78±6	1.22± .06

[a] Extrapolated relative absorptivities employed for 1.0(OCH_3/C_9), G_c=1.0, are: .43, .34, 0, .64, and .57, respectively for 1600, 1460, 1325, 1220, and 1115 cm^{-1}; from Sarkanen *et al.*.[17]

[b] Extrapolated relative absorptivities employed for 2.0(OCH_3/C_9), S_c=1.0 are: 2.128, 1.68, 1.30, 1.67, and 3.36, respectively for 1600, 1460, 1325, 1220, and 1115 cm^{-1}; from Sarkanen *et al.*.[17]

[c] Averages of %G and OCH_3/C_9 include data obtained at 1600 and 1115 cm^{-1}.

[d] Extractives free.

of 10-20 pulses. The spectral width was 900 or 1000 Hz with 450 or 500 Hz filter respectively. The integration of lignin spectra was checked against that of lignin model compounds obtained under similar conditions. From the hydrogen content of the samples (elemental analysis) and from the distribution of protons in the NMR spectra, the approximate number of protons per C_9 unit was calculated for aromatic, aliphatic, and hydroxy protons (see Table 4). The methoxy protons overlap with some side-chain protons; therefore analytical values for methoxy protons were subtracted from the aliphatic region to determine the number of aliphatic protons per C_9 formula.[20]

The ^{13}C NMR spectra reported here used the pulse sequence described in reference 12 with antigate decoupling proton technique, such that the nuclear Overhauser effect could be overcome. Pulses of 10 μs were employed with a 10.0 s interval between pulses for a total accumulation of 20,000 pulses. The long delay time is necessary to correct for the different spin lattice relaxation times of the various types of carbon present in the lignin molecule.

RESULTS AND DISCUSSION

Characterization and Analytical Results

Voltammetric studies of ethanol-extracted explosively-depressurized aspen lignin (EEEDAL) at a hanging mercury drop electrode indicate that a number of electrochemical processes occur in methanol/tetraethylammonium perchlorate (TEAP) supporting electrolyte (see Fig. 1). At around -1.8 V vs. Ag/AgCl, processes probably are associated with *o*-quinone reduction to hydroquinone.[21] Additional reduction reactions take place at -2.6 V *vs*. Ag/AgCl, which was the potential chosen to carry out constant potential electrolyses of EEEDAL. Under these conditions direct electrochemical reductions and indirect reductions involving the participation of the reduced form of the alkylammonium ion asso-

Table 4. Integrated ^1H NMR regions roughly proportional to the types of protons per C_9 formula (except OCH_3 values which were derived from analysis) of EEEDAL and lignin samples described in Table 1. (All data from acetylated lignins corrected for extractives.)

Sample	Aromatic	Aliphatic Side Chain	OCH_3	OH*	Total
EEEDAL	2.2	4.0	3.6	1.7	11.6
FAS-12	2.1	3.9	3.9	1.8	11.8
EFAS-12	2.7	4.2	3.6	2.0	12.6
FAI-12	2.2	3.9	3.3	1.6	11.0
EFAI-12	2.9	3.3	3.3	1.6	11.2
FAI-7	2.7	3.8	3.45	1.7	10.7

*Includes highly shielded protons from Hibbert ketone structures.

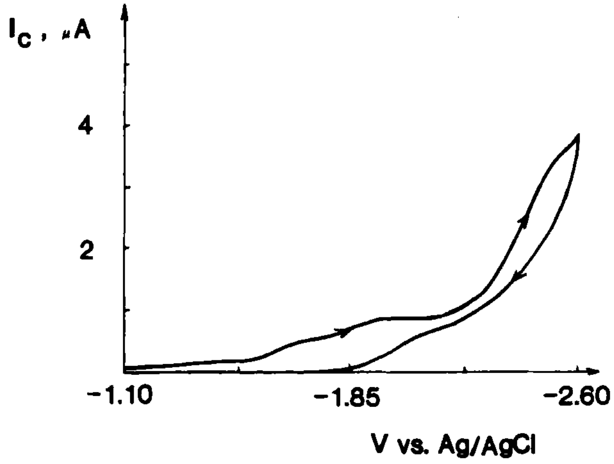


Figure 1. Cyclic Voltammogram of EEEDAL (6.7 mg/5cm^3) on a Hanging Mercury Drop in $CH_3OH/(C_2H_5)_4NClO_4$(0.1 mol dm^{-3}.)

ciated with mercury are likely. We will describe results of electrolytic experiments performed on mercury pool cathodes after passing 2900 C of charge/3 g lignin. The pH of the catholyte in these electrolyses rises very quickly to 12 (within the first 5 minutes) and remains constant throughout the electrolysis (1-3 hours).

The different conditions employed in the isolation of the lignin materials used in this work, and their yields are presented in Table 1. The fractionation procedure was developed in order to allow maximum recovery of the starting lignin material after electrolysis. In order to assess the effect of the electrolysis on the polymer distribution and composition, the same fractionation procedure was employed, but without electrolysis. Also clear from Table 1 is that the distribution of the polymer in AI, AS, and VS fractions is a function of the starting pH of the methanolic solution. Under the electrolysis conditions employed we observed an increase in the yields of the AS and VS fractions and a decrease in the yield of AI fraction.

Table 2 shows the elemental composition, methoxy, carbonyl, and total hydroxy contents of the various lignin preparations described in Table 1. Note that the presence of extractive impurities in the lignin materials increases the C and H contents of the lignins, and decreases the methoxy content. The proportions of the various groups are described by the C_9 formulae in the table in terms of $C_9H_XO_Y(O_{CO})_Z(OH)_M(OCH_3)_N$. The agreement between the C_9 composition of the acetylated and unacetylated EEEDAL is well within the experimental error. The compositions of the acid-insoluble fractions are subjected to the largest errors since the fatty acids and fatty alcohols will be predominantly present in this lignin fraction.

The range of methoxy content, 1.1-1.3 OCH_3/C_9, is lower than the value reported by Chua and Wayman[22] for the milled wood aspen lignin $[C_9H_{8.7}O_{3.05}(OCH_3)_{1.47}]$. The reported values of 0.95-1.15[2d] or 1.1[2c] for analogous materials are closer to the values of our AI fractions. From the data of OCH_3/C_9 in Table 2 it appears that the AS fractions have a slightly higher OCH_3 content than the AI fractions. These trends are substantiated by the IR data (see Fig. 2) treated according to the method of Sarkanen _et al_.[19] Table 3 contains the evaluation of the OCH_3/C_9 ratio as well as the guaiacyl content (G_c). The ratios of the absorbances of individual maxima (e.g., 1600, 1460, 1325, 1220, and 1115 cm^{-1}) relative to that at 1500 cm^{-1} are compared to extrapolated values of Sarkanen _et al_.[19] for 1.0 and 2.0 OCH_3/C_9, respectively for lignins containing 100% guaiacyl (G_c=1.0) and 100% syringyl units (S_c=1.0):

$$\begin{vmatrix} 1 \\ A_i/A_{1500} \end{vmatrix} = \begin{vmatrix} 1 & 1 \\ (A_i/A_{1500})_{G_c=1} & (A_i/A_{1500})_{S_c=1} \end{vmatrix} \times \begin{vmatrix} G_c \\ S_c \end{vmatrix}$$

assuming: $S_c = 1-G_c$, _i.e._, the amount of p-hydroxyphenylpropane units in the EEEDAL is negligible (see experimental part for estimate of p-hydroxyphenyl propane units). The average OCH_3/C_9 values and the guaiacyl content from Table 3 compare very well with those from Table 2. The presence of extractives does not seem to alter the methoxy content determination by this procedure, within the experimental error.

The decrease in the methoxy content reflects condensation reactions of the lignin with furfural, the acid degradation product of the xylan fraction, formed during the explosive decompression of the wood. Such condensation products seem to be predominantly present in the AI fractions.

The carbonyl content of EEEDAL prior to or after fractionation decreases markedly during electrolyses at −2.6 V _vs_. Ag/AgCl. At the same time, the total hydroxy and the hydrogen contents increase as depicted in Table 2. The very soluble fraction remaining after the electrolyses has not been isolated from solution without appreciable contamination by the supporting

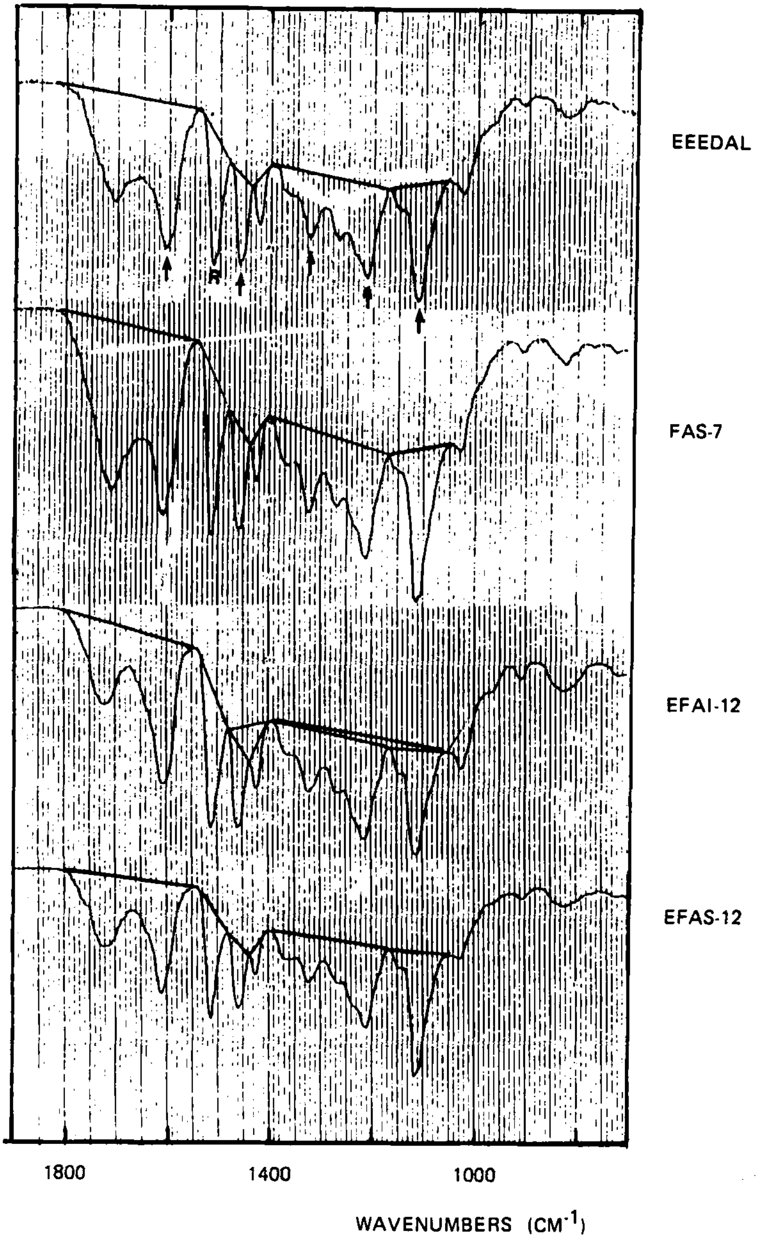


Figure 2. Infrared Spectra of Selected Lignin Samples (see Table 1) in KBr Pellets.

electrolyte. However, its carbonyl content is also very low (0.8% by weight or less) and its phenolic OH content, determined by UV-visible difference absorption spectra[15] is at least as high as that of the acid-soluble fraction.

Table 5 presents the empirical formulae corresponding to the C_9 formulae of Table 2, and the double-bond equivalent number (DBE) of the various lignin preparations. Whereas the milled wood aspen lignin[22] (MWAL) presents a DBE of 3.9, EEEDAL has a higher value (4.5). The DBE's after fractionation are lower in the FAS and higher in the FAI fractions respectively. Both DBE's decrease proportionally after electrolysis; the EFAS value is identical to that of the MWAL and the EFAI is still higher, indicating that this fraction may have more condensed structures.

Table 6 presents the assignment of major ^{1}H NMR peaks as well as the peaks of the CCl_4 extracted fraction of the acetylated EEEDAL. The distribution of the protons in the NMR spectra of the acetylated derivatives of the lignins described in Table 1 (except the VS fractions) was determined following the method of Ludwig _et al._[19] Due to the overlap of methoxy protons with other side-chain protons, the analytical value for the methoxy protons was used, and subtracted from the integrated 3.2-6.2 ppm region in order to assess the aliphatic proton content. One major difference between these spectra and the majority of published MWL data (e.g., ref. 23) is that the aromatic acetate region is much more pronounced than the aliphatic acetate, indicating a higher phenolic OH content than alcoholic OH content for the EEEDAL and lignins described in Table 2. Table 4 presents results on the distribution of the various types of protons and the total OH content (aromatic and aliphatic). The hydroxy contents by proton NMR are 20-40% higher than those obtained by chemical analyses or ^{13}C NMR determinations (see Table 7). Higher results reflect the presence of non-extracted materials, as well as the larger number of γ-methyl groups in the Hibbert ketones acid hydrolysis products which have intense peaks in this region. Proton NMR measurements

Table 5. Empirical formulas and number of bond equivalents (DBE)[a] of EEEDAL, and lignin samples described in Table 1.

Sample	Empirical Formula, $C_AH_BO_C$	DBE[a]
EEEDAL	$C_{10.1}H_{11.5}O_{3.7}$	4.4 ± .05
FAS-12	$C_{10.3}H_{11.6}O_{4.5}$	4.5 ± .2
EFAS-12	$C_{10.2}H_{12.6}O_{3.9}$	3.9 ± .1
FAI-12	$C_{10.1}H_{11.0}O_{3.4}$	4.6 ± .1
EFAI-12	$C_{10.1}H_{11.9}O_{3.1}$	4.2 ± .1
FAS-7	$C_{10.2}H_{11.5}O_{4.1}$	4.5 ± .1
FAI-7	$C_{10.2}H_{10.5}O_{3.6}$	4.9 ± .1

[a] The double bond equivalent is calculated as (2 × A × 100 + 2 − B × 100)/2.

Table 6. Assignment of signals in the ^1H NMR spectrum of acetylated ethanol-extracted, steam-exploded aspen lignin. Several peaks are broad and have irregular shapes. δ values given refer to the highest point of the peak or to shoulder (s).

δ Value, ppm	Assignment
9.90	Formyl protons in benzaldehyde units
7.28	Chloroform solvent
7.51 (sharp)	Aromatic protons located <u>ortho</u> to carbonyl group
7.15 (sharp)	Traces of toluene - Aromatic protons
6.97 (broad)	Aromatic protons in guaiacyl units
6.60 (broad)	Aromatic protons in syringyl units
6.03 (broad)	H_α in β-O-4 and β-1 structures
5.33	Largely from extractives;* possibly phenylcoumaran structures
4.56	H_β in β-O-4 structures
4.25, 4.38	H_γ in several configurations
3.83 (3.72s, 3.89s)	Protons in methoxy groups plus H_γ side chain contributions
2.31	Aromatic acetate
2.04	Aliphatic acetate
1.26, 0.89	Highly shielded aliphatic protons; also contains protons from the extractives*

*Lignin with low content of extractives from aspen. The EEEDAL was extracted in CCl_4. ^1H NMR spectrum of the extracted fraction is: .878 multiplet; 1.255; 1.312; 1.599 triplet; 2.018 broad; 2.317 broad multiplet; 2.766 triplet; 4.149 quartet; 5.34 quintet.

Table 7. Types and approximate proportions of OH groups/C_9 formula derived from chemical analyses and NMR analysis of the EEEDAL and lignin samples described in Table 1.

Sample	Total OH Analysis	OH_{phen}	OH_{aliph}
EEEDAL	1.2	0.72[a] 0.68[b]	0.48[a] 0.54[b]
FAS-12	1.3	0.86	0.44
EFAS-12	1.4	0.80[a] 0.90[b]	0.63[a] 0.60[b]
FAI-12	1.1	0.64[a]	0.46[a]
EFAI-12	1.1	0.6 0.5	
FAS-7	--	0.9 --	
FAI-7	1.15	0.63	0.52

[a] Analytical data only, i.e., total OH determined by methylation followed by OCH_3 determination according to reference 11; phenolic OH determined by conductimetric method.

[b] From ^{13}C NMR

of hydroxyl content are usually 20% higher than other analytical methods.[23]

The phenolic and alcoholic OH contents are assembled in Table 7. Confirming the ^1H NMR spectra, the phenolic OH content is higher than the aliphatic OH content for all lignins investigated in this work. Whereas FAI and EFAI lignins have a lower phenolic OH than EEEDAL, the FAS, EFAS, FVS, and EFVS have a much higher phenolic OH content, approaching unity/C_9. Whereas a marked increase in aliphatic OH content is observed in going from FAS to EFAS and from FAI to EFAI, the phenolic OH contents remain constant to within the experimental error. However, since the effective amount of EFAS + EFVS is higher than that of FAS + FVS, overall we also observe a modest increase in phenolic OH content in the acid-soluble lignins (AS + VS)(See Table 1).

Figure 3 compares the acetate ($>C=O$) region of the ^{13}C NMR spectra of EFAS and EFAI. Primary, secondary, and aromatic ace-

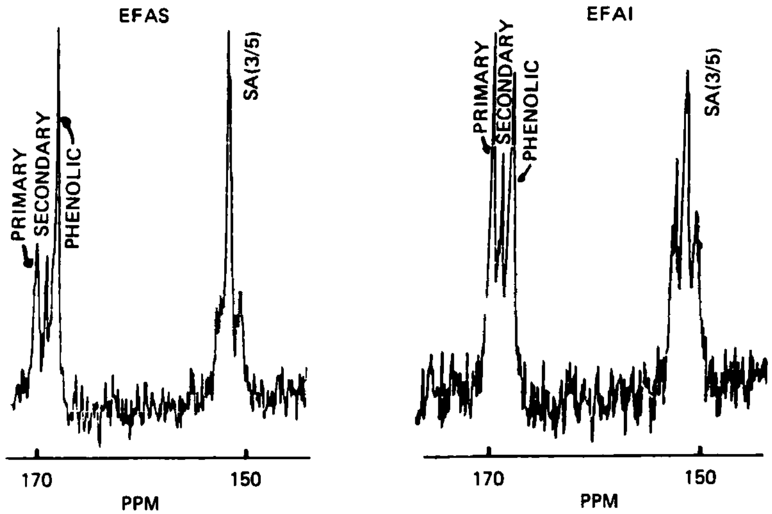


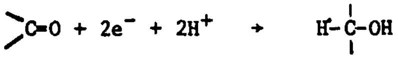
Figure 3. ^{13}C NMR Spectra of Acetylated EFAS-12 and EFAI-12 in the 150-170 ppm Range. [S_A (3/5) = carbons in positions 3 and 5 of acetylated syringyl groups.)

tate peaks can be seen from these spectra as well as the marked differences in the distribution of these OH groups in the fractions. Increases in both primary and secondary hydroxy groups are observed after electrolysis. A more pronounced increase is obtained in going from FAS to EFAS suggesting that this fraction had a larger amount of Hibbert-ketone type products (see below).

Exhaustive Electrolysis

The electrolyses experiments described in this work consumed 2900 C of charge/3 g of lignin. Since the constant potential at which the reduction was carried out is close to the end of the useful electrochemical cathodic window of the methanol/tetraethylammonium perchlorate solvent system, the analysis of the charge consumed needs to take the solvent decomposition into account (H_2 evolution). Assuming that the background current is unchanged by addition of the lignin, one can calculate the charge associated with this reaction. This assumption is reasonable since in these electrolyses the current decreases exponentially to a value close to that of the background current at which point the electrolysis is interrupted. The background reaction charge consumption was estimated as $(1.0 \pm 0.2 \times 10^3)$C.

From the analytical results shown in Table 2, a major electrochemical reaction is the reduction of carbonyl groups to hydroxy groups (either directly or through the participation of the reduced ammonium salt):



$$>C{=}O + 2e^- + 2H^+ \rightarrow H{-}\overset{|}{\underset{|}{C}}{-}OH$$

which consumes 2F/mol of carbonyl groups. The consumption of charge for carbonyl groups of 3 g of lignin is 700-900 C (average of several electrolyses).

The acid hydrolysis of the lignins during the explosive decompression leads to an increased free phenolic content due to the cleavage of β-O-4 alkyl-aryl ether bonds. In addition, α-O-4 alkyl aryl ether bonds or bonds between the lignin and the hemicellulosic fraction are also easily hydrolyzed under these conditions. Therefore α-hydroxy groups are liberated.

The carbonyl compounds formed under acid hydrolysis conditions are the Hibbert ketones, which could be reduced under the present electrolytic conditions. Lundquist[26] reviews the low-molecular weight lignin acid hydrolysis products. The more likely low-molecular weight products which could be reduced under these conditions include: G- or S-CH_2COCH_3; G- or S-$COCOCH_3$; G- or S-CHOH CO-; G- or S-CO-CHOH-; G- or S-CH_2CHO; G-CH=CH-G or S; [G = guaiacyl and S = syringyl group]. Benzyl ether structures would also be reduced. Estimates of their possible concentration would lead to a consumption of ~20 C.

Units in which carbonyl groups are adjacent to β-O-4 alkyl aryl ether bonds are activated for ether bond reduction, as observed by Zuman in related compounds. In fact, a model compound such as G-CO-CH_2O-G presents reduction waves at a hanging mercury drop electrode at about -2.1 and -2.4 V vs. Ag/AgCl in methanol/tetrabutylammonium perchlorate supporting electrolyte, waves that are very close to the background (as observed for the lignin). Ether cleavage is observed in the reduction,[25a] confirming results of Russian workers.[25b] It is interesting to notice that in methanol, for model compounds containing free phenolic groups, the reduction waves occur at much more negative potentials than if the phenolic groups are protected by benzyl or methyl groups.[25a] [For instance, for the O-benzyl derivative two waves are observed at -1.47 and -1.77 V vs. Ag/AgCl with slopes of the log $i/(i_L-i)$ plots of ~70 and 270 mV/decade; upon reduction at -2.3 V vs. Ag/AgCl guaiacol and benzyl alcohol were detected.]

Additionally, since at -2.6 V vs. Ag/AgCl, conditions close to solvated electron formation are achieved, it is possible that β-O-4 ether linkages are cleaved. For a two-electron process, the remainder of charge [3000-1000-(700 to 900)-20] = 1280-1080 C corresponds to about 6-7 mmoles of reducible groups.

The cleavage of the β-O-4 alkyl aryl ether bonds would lead to an increase in the fragmentation of the polymer and cause an increase in the amount of acid-soluble and very-soluble fractions and in the phenolic OH content, both of which are observed. During the electrolyses at pH 12 it is possible that at the level of the electrode base-promoted conjugate additions could have taken place to some extent. Our subsequent studies at controlled pH (<9) indicate that no condensation reactions occur but only depolymerization.[27] The condensation reactions could involve quinone-methide or side-chain enone structures and carbanions from the phenolic or enolic units.[28] Such condensation reactions could lead to the observed increase in number-average molecular weight. The molecular weight distribution of EEEDAL and of the fractions obtained after fractionation have been described.[29] From the high-performance size exclusion chromatograms obtained after electrolysis (EFAI to EFAS), one can obtain their weight-

Table 8. Molecular-weight distribution of EEEDAL compared to those of selected lignin samples described in Table 1.

Sample	$\bar{M}_w$	$\bar{M}_n$	Polydispersity	Reference
EEEDAL	1980	925	2.1	29
FAI	2130	1070	2.0	29
EFAI	2250	1480	1.5	this work
EFAS	1430	1000	1.4	this work

average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weight as well as the polydispersities ($\bar{M}_w/\bar{M}_n$) for the fractions isolated after electrolysis compared to those obtained after fractionation. Table 8 compares these data for the polydisperse materials EEEDAL, FAI, EFAI and EFAS. FAS exhibits paucidispersity (distinct monomers, dimers, trimers,and tetramers); a rough estimate of the polydisperse fraction gives for $\bar{M}_w$ and $\bar{M}_n$ $\sim$1400 and $\sim$750, respectively. After electrolysis all the chromatograms are characteristic of polydisperse materials. These data suggest that electrolysis decreases the polydispersity of the lignins from $\sim$2 to $\sim$1.5. As ether bonds are cleaved, lower molecular weight entities are generated, thus explaining the change in fragmentation pattern (changes in the amount of polar OH groups would also affect the fractionation pattern). The remaining insoluble fraction has a higher number average molecular weight probably due to electrochemical coupling reactions.

CONCLUSION

The ethanol-extracted explosively-depressurized aspen (*Populus tremuloides*) lignin (EEEDAL) has been characterized with respect to its functional group composition and reductive electrolysis in methanol/tetraethylammonium perchlorate solvent system. A fractionation procedure was developed to recover a large fraction of the lignin by differential solubility in aqueous acid solution. Two different types of lignins are isolated under these conditions prior to electrolyses: (1) An acid-insoluble material with a phenolic OH content ~10% smaller than that of the original EEEDAL, and similar aliphatic OH content. This material has a higher double-bond equivalent and appears to be more condensed than the acid soluble fractions. (2) An acid-soluble fraction which has a phenolic content approaching 1 per C_9 formula and a similar alcoholic OH content. After electrolyses the amount of low molecular weight acid soluble materials of high phenolic OH content increases, as well as the alcoholic OH content of all the fractions, indicating cleavage reactions and carbonyl group reductions. One major effect of electrolyses is on the molecular weight distribution of the resulting polymers. Whereas the starting material (or fractionated materials) have polydispersity of ~2, the reductively electrolyzed materials have a polydispersity of 1.5. Carbonyl reduction, β-O-4 alkyl ether reductive cleavage, and reductive couplings are the major reactions compatible with the analytical results and the molecular weight distribution observed.

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