

ELECTRICAL ENERGY FROM INDUSTRIAL LIGNIN: A PRELIMINARY EVALUATION¹

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ABSTRACT

Kraft lignins can be pyrolyzed to durable, electrically conducting solids. These pyrolysates are able to function as cathodes in metal-lignin batteries. Voltage-time characteristics and fuel cell capabilities are discussed: results show sufficient promise to warrant further study.

Additional keywords: Pyrolyzed lignin, zinc-lignin batteries, redox properties, voltaic cells, kraft lignin utilization.

Despite several decades of intense applied research into the properties of lignin, uses have been found for only a small portion of the many millions of tons of lignin that accumulate annually as a by-product of the wood pulp industry. A few specialty chemicals, such as vanillin and dimethyl sulfoxide, are derived from lignin, but these constitute a very small fraction of the total annual production. A large fraction of the commercial lignin is burned as an industrial fuel. Hardly any of the commercial byproducts take advantage of the highly organized structure of the lignin macromolecule.

Kraft and alkali lignins contain quinone-hydroquinone structures in the macromolecule (Steelink 1966; Tollin and Steelink 1966). As such, they represent potential sources of electrical energy, in particular, as regenerative electrodes for primary batteries. If these lignins could be made conductive, one might obtain materials that could be used in a number of stationary power supplies, such as signal devices, emergency power for buildings, railroad switching devices, and many other examples. The market for such power supplies would not absorb the bulk of the lignin production, but it could create another outlet for the specialty uses of lignin.

In addition to its redox properties, alkali lignin possesses a number of properties that

favor usage as a potential cathode in a battery. These are:

1. It is thermoplastic and can be molded.
2. After it is pyrolyzed, it becomes conductive.
3. After pyrolysis, it is a cohesive solid that maintains its shape and is fairly resistant to mechanical shock.
4. It is functionalized and therefore can be chemically modified prior to pyrolysis.
5. It is abundant and cheap.

All of the above prompted us to examine some industrial lignins as potential cathodes in voltaic cells. The use of organic materials for voltaic cells is not new, of course. Quinone-hydroquinone monomers, when mixed with conducting charcoal and resins, perform quite well in metal-organic voltaic cells (Glicksman and Morehouse 1959). Another type of cell has attracted considerable attention: the metal-air battery. This cell utilizes a special charcoal-noble metal cathode that catalyzes the reduction of oxygen (Collins 1971; Mantel 1970; Schumacher 1971). Other experimental cells use quinone materials that can be regenerated by air (Sandstede 1972). All of the organic components in the above batteries are fairly exotic and expensive.

In theory, lignin should be able to perform the cathodic functions of the batteries described above. The following exploratory experiments were carried out to test this assumption. They represent a material eval-

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uation, in which different industrial lignins were subjected to heat and chemical modification. These experiments do not include engineering studies, which would be required to convert a suitable electrode material to an economic battery.

EXPERIMENTAL AND RESULTS

Redox properties

Hardwood and softwood kraft lignins² were dissolved in aqueous alkali and placed in separate compartments. These were connected by a salt bridge, fitted with platinum charge collectors and charged overnight with a DC voltage of 2 volts. This wet assembly was able to hold a charge and discharge through a load for one hour. Although this is a cumbersome device, it did confirm our earlier prediction that lignin possesses redox functionality, which is capable of delivering electrical energy.

Pyrolysis

A number of kraft lignins were heated in an atmosphere of nitrogen to temperatures up to 1000 C. The pyrolysates were low density solids. If the pyrolysis temperature was raised above 600 C, the materials became electrically conducting (i.e., resistance less than 5 ohm/cm). The pyrolysates had good mechanical strength and could be machined, drilled, or sanded. A material of superior mechanical strength could be obtained by mixing powdered pyrolysate with untreated lignin and repyrolyzing the mixture.

Chemical modifications

A number of simple chemical modifications were carried out with softwood kraft lignin in an attempt to improve the oxidation potential and conductivity. Also, we were interested in determining the extent of incorporation of certain elements into the lignin macromolecule. Subsequent to the chemical treatment, all of the products were heated to 800 C for one hour under nitrogen. The following experiments were carried out.

² Kindly donated by WestVaco, North Charleston, South Carolina.

a. Softwood lignin³ (Product A) was stirred with dilute nitric acid for two days. The mixture was filtered, the precipitate dissolved in aqueous ammonia and the nitrated ammonium lignin salt recovered by evaporation to dryness at room temperature (Product B).

b. Softwood lignin (A) was stirred with dilute nitric acid for two days. The mixture was filtered, the precipitate dissolved in 25% aqueous NH_4S_x , warmed to 80°C and then evaporated to dryness (Product C).

c. Product B was dissolved in an aqueous solution of $\text{Cr}(\text{NO}_3)_3$. The resulting precipitate was filtered, washed and dried (Product D).

Pyrolysate Products A–D were analyzed for the elements C, H, N, S, and Cr. Conductivity measurements were made on the powdered samples. These data are shown in Table 1.

The results show that even at 800 C, the pyrolysate retains a large residue of functionality. Under mild conditions of chemical treatment, N, S and transition metal are incorporated and retained at high temperature.

Conductivity can be drastically altered by chemical modification. The resistance values shown in Table 1 are much higher than those for solid blocks of material. For example, Lignin B has a resistance of 2 ohms when in the solid form, as compared to 155 ohms under powdered conditions. No doubt, contact is poor between powder particles; however, comparison under standard conditions is easier with powders than with solid blocks.

Cathode behavior

To test the pyrolysates as potential cathodes, we constructed a simple voltaic cell. The anode was a 1 cm² square of zinc sheet (1.25 grams). The cathode was a disc of pyrolysate, 2.0 cm. in diameter weighing 2.0 grams. The two electrodes were separated by an asbestos sheet soaked in an electrolyte (usually saturated NH_4Cl). A wick connected the asbestos sheet to a

³ Kindly donated by Domtar Research Center, Montreal, Canada.

TABLE 1. *Properties of modified lignin pyrolysates*

Lignin Sample	Elemental Analysis					Resistance ^a Ohms
	C	H	N	S	Cr	
A	85.23	1.22	-	-	-	170
B	79.15	1.37	6.55	-	-	155
C	69.09	0.71	6.18	4.43	-	88
D	71.44	0.89	4.01	-	10.31	16

^aResistance measured across a cylinder of powder, 1 cm. X 0.2cm², packed under 1.0 lb. pressure. Powder to pass 80 mesh screen or less.

well of electrolyte solution. Voltages across the zinc-pyrolysate electrodes were measured at various time intervals and recorded as shown in Table 2. The voltage V_L was measured across a load of 100 ohms, which corresponds to the load of a small lamp. Indeed, these batteries developed enough power to light a small bulb for one half hour, or until the voltage dropped below 1.0 volt.

Catalytic reduction of oxygen

The recovery cycle of these cells suggested that the lignin cathode might be catalyzing the reduction of molecular oxygen in the air. To test this assumption, we measured the voltage of the lignin A cell while the latter was encased in a nitrogen bag. Under these conditions, the V_{oc} was 0.71 volt and the V_L was 0.42-0.29 volts (compare to 1.22, 1.00-0.53 in air). The original voltages were restored when the

cell was placed in air. Thus the pyrolysate had surface properties somewhat comparable to commercial renewable cathodes, made from conducting charcoal impregnated with noble metal and resin.

Comparison to commercial dry cell

For a performance comparison to a single Eveready Dry Cell (1.5 volt), we constructed a 65 gram lignin pyrolysate block. When this was wrapped with impregnated asbestos and zinc sheet, it approximated the size of a dry cell. The voltage properties of this assemblage were: $V_{oc} = 1.24$; $V_L = 1.20-1.04$ (2 hours discharge). Under the same conditions, the Eveready Cell (85 grams) performed as follows: $V_{oc} = 1.50$ volts; $V_L = 1.48-1.44$.

CONCLUSION

Lignin pyrolysates are capable of functioning as cathodes in voltaic cells. They

TABLE 2. *Lignin-zinc cell voltages*

Lignin Sample	V_{oc}^a	V_L^b	Recovery Period	V_L^c
A	1.22	1.00-0.53	12 Hours	0.91-0.46
Tomlinite ³	1.24	0.50-0.17	"	0.44-0.10
B	1.39	1.06-0.73	"	1.04-0.68
Hardwood Kraft ²	1.24	1.04-0.53	"	1.06-0.50

^aOpen circuit voltage.

^bVoltage measured across 100 ohm load. First number is initial voltage; final number is voltage after two hours discharge under load.

^cVoltage across 100 ohm load after recovery period, measured as for V_L^b .

are susceptible to simple chemical modification prior to pyrolysis: these modifications dramatically alter their electrical properties. Because of the thermoplastic nature of lignin and its chemical modifications, solid cohesive electrodes can be cast in a number of desirable configurations. In addition, the pyrolysates appear to have catalytic surface properties that promote the reduction of oxygen at room temperature. These could be optimized by appropriate modification experiments. If such a surface could be achieved, one would obtain a truly renewable (or permanent) electrode: i.e., a fuel cell using only air for the cathode.

At present, these crude zinc-lignin batteries represent only a feasibility study. Certainly, they do not compare to commercial dry cells. But they do perform well enough to justify further study. In this exploratory work, a number of parameters have been identified. These will constitute the basis for a systematic investigation of

the electrochemical properties of alkali lignins.

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