

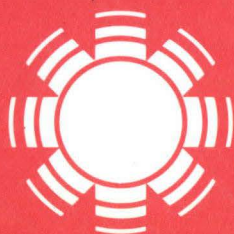
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December 1982

Survey of the Electrochemistry of Some Biomass-Derived Compounds

Helena L. Chum
Solar Energy Research Institute

Robert A. Osteryoung
State University of New York at Buffalo



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Solar Energy Research Institute

A Division of Midwest Research Institute

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Prepared Under Task Nos. 3356.10 and 3356.50

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PREFACE

This survey was prepared by R. A. Osteryoung, formerly with Colorado State University and now with the State University of New York at Buffalo, and by H. L. Chum, formerly with Colorado State University and presently on the SERI staff. Work was performed partly under Contract No. AM-9-8078-1 and SERI tasks 3356.10 and 3356.50. This review covers the technical background of the electrochemistry of biomass-derived materials such as selected polysaccharides and monosaccharides, lignins, and pyrolysis chars of lignins and related compounds. Emphasis is placed on synthetic work. However, whenever applicable, the work on fuel cells for power generation using such compounds is reviewed as well.

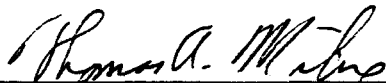
The authors wish to acknowledge the aid of T. A. Milne and C. S. Smith in suggesting this report and for helpful discussion. Helpful discussions with Forest Products Laboratory members J. Harris, L. Landucci, T. Jeffries, E. Springer, and with SERI staff--in particular K. Grohmann--are acknowledged. The criticism and suggestions from M. Baizer, S. Brummer, J. Giner, E. Sjöstrom, H. Schroeder, H. Silverman, D. Sopher, and N. Weinberg are greatly appreciated.



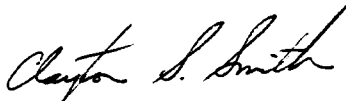
Helena L. Chum
Senior Electrochemist

Approved for

SOLAR ENERGY RESEARCH INSTITUTE



Thomas A. Milne, Chief
Thermochemical and Electrochemical
Research Branch



Clayton S. Smith, Manager
Solar Fuels and Chemicals Division

SUMMARY

This report is a literature survey of the electrochemistry of selected biomass-derived compounds. The term biomass represents all plants, whether grown on land or in water, and includes crop and forest residues. Urban and industrial wastes or animal residues can also be considered biomass. Only the main polymeric components of biomass, which account for a large proportion of the total biomass (e.g., >95% of wood), are surveyed. The polymers cellulose, hemicelluloses, starch, and lignin are reviewed, as well as selected monosaccharides and chars of lignins. The objective of this report is to aid evaluations of electrochemical conversion of biomass-derived compounds into energy-intensive chemicals, petrochemical substitutes, useful chemicals, and electricity.

The electrochemical reactions of the selected biomass-derived compounds are reviewed with emphasis on the synthesis of chemical compounds and electric power generation in fuel cells whenever applicable.

Chemicals successfully synthesized electroorganically from mono- and polysaccharides include dialdehyde starch, aldonic acids, and polyalcohols. In general, such syntheses aim at speciality chemicals. Fuel cells employing poly- and monosaccharides generate low power densities in the aqueous solutions investigated (neutral, alkaline, and acid) under 90°C. The research described did not fully utilize well-developed technology for fuel cell electrodes and catalysts. Emphasis of the research has been in special applications such as glucose sensors and implantable cardiac pacemakers.

With regard to electrochemical oxidation or reduction of lignins of different species and in different media, some of the research emphasis has been on the production of low-molecular-weight carboxyl- and carbonyl-containing compounds as well as of modified lignins with suitable physicochemical properties for polymer applications. Reductive degradation experiments led to the synthesis of monomeric and dimeric phenolic units. Analytical applications of electrochemical techniques are reviewed and applied to lignins. The use of electrochemical delignification in the pulp and paper industry is also briefly covered.

Pyrolysis of lignins produces thermoplastic materials with semiconducting properties. Their possible uses as electrodes or depolarizers are reviewed. Because these chars are analogous to coke materials, review of some of the electrochemistry of direct and indirect fuel cells using coke materials is included.

The electrochemical production of energy-intensive chemicals or petrochemical substitutes from biomass-derived compounds has not been addressed in the literature. Recommendations for future research are made which encourage the electrochemical research of polymeric materials resulting from newly developed pretreatments of biomass, such as explosive decompression and organosolv pretreatments of wood. Because lignins are the only renewable source of phenolic compounds, electrochemical research of these materials is strongly encouraged.

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SECTION 1.0

INTRODUCTION

1.1 OBJECTIVE

This survey of the electrochemistry of some biomass-derived compounds was written at the request of T. A. Milne and C. S. Smith of the Solar Fuels and Chemicals Research Division of the Solar Energy Research Institute. The purpose of this review is to aid evaluations in the field of electrochemical conversion of biomass-derived compounds into energy-intensive chemicals (fuels and fuel additives), petrochemical substitutes, useful chemicals, and electricity. The rationale for investigating these electrochemical transformation routes is to provide a means to store electrical energy in the easily transportable liquid fuels derived from biomass after electrochemical processing, and to upgrade by-products of biomass processing. These routes assume the availability of affordable electrical energy, to be derived in the future from solar sources such as photovoltaics, solar thermal collection, and hydroelectricity (whenever applicable), and from nuclear sources. Affordable electricity is presently available in a number of countries in which hydroelectric and/or nuclear power are abundant. In many cases--e.g., for petrochemical substitutes and for valuable organic chemicals (albeit of small volume)--the present economics of production using electricity derived from coal, hydroelectric energy, or nuclear energy is already favorable. An impressive example is the production of adiponitrile from acrylonitrile by electrohydrodimerization. This process was developed by Baizer (1965) and is used by Monsanto to produce 2×10^8 kg/yr in the United States and the United Kingdom (Danly 1980).

The scope of this report is restricted to the evaluation of the basic polymeric biomass-derived materials--cellulose, hemicelluloses, starch, and lignins--and of a few selected compounds derived from these polymers. A later publication will evaluate electrochemical conversion of biomass materials derived from microbiological, chemical, and thermochemical pretreatments.

We review systems investigated in the past. The information comes from literature searches. In some cases we did not have access to the original literature, principally that of Soviet origin, and the description of the work is based on abstracts from Chemical Abstracts (CA) and/or the Abstract Bulletin of the Institute of Paper Chemistry (IPC).

1.2 BACKGROUND

In the strictest sense, biomass refers to organic matter produced by plants. The habitat of the living organisms can be terrestrial or aquatic, thereby defining terrestrial and aquatic biomass. In a less strict sense, biomass can be defined as the material that results from direct or indirect photosynthetic processes. According to this definition, animal residues and urban and industrial wastes can also be considered biomass. The latter two sources of biomass cannot be ignored as a resource since they contain as much as 50% cellulose. Biomass of animal origin is not treated in this report.

Fortunately for the prospect of converting biomass into chemicals, the composition of biomass is not as varied as its morphology. Plant cell walls comprise as much as 95% of the plant material. Therefore, the polymer components of the cell walls--cellulose, hemicelluloses, and lignin--provide the feedstocks for most of the chemicals attainable, thus simplifying the field of biomass conversion. Other biomass components include extractives, vegetable oils, starch, etc. (Goldstein 1980).

In this report, the electrochemistry of the basic polymeric materials--cellulose, hemicelluloses, starch, and lignins--is reviewed. Emphasis is given to synthesis work aimed at the production of chemicals. However, when applicable, work related to electric power generation in fuel cells utilizing these biomass-derived materials is reported. The literature coverage is restricted to searches of Chemical Abstracts, the Abstract Bulletin of the Institute of Paper Chemistry, and the Bibliography of Electro-organic Synthesis 1801-1975 (Swann and Alkire 1980).

The field of electroorganic synthesis originated in the last century with studies of the electrolyses of alcohols (Reinhold 1802). In 1834, Faraday performed the first electrolyses of carboxylates yielding hydrocarbons, which were more thoroughly investigated and popularized by Kolbe (1847). This field has expanded greatly since that time. Syntheses can be carried out by electrolytic oxidation, reduction, cathodic or anodic coupling, substitution, elimination, etc. (see Baizer 1973; Weinberg 1975; Fry 1972; Ross et al. 1975; Tomilov 1972). Examples of the wealth of data are the first comprehensive bibliography by Fichter (1942) and its sequel by Swann and Alkire (1980), the latter with over 12,000 references from 1801 to 1975.

Electroorganic synthesis can offer a greater selectivity of products than the corresponding chemical processes, principally reductive processes. This is due to the fact that in electrochemical processes, in addition to the normal variables of chemical reactions (medium, temperature, pressure, pH, catalyst, and time), the following variables are added: electrode materials, electrode potential, current density, solution conductivity, and cell design. Advantages of electroorganic synthesis include

- the control of the oxidizing or reducing power of the electrode;
- the ability to perform electrolyses at various temperatures, but usually near or at room temperature;
- the ability to perform several chemical steps in one electrochemical step;
- the ability to form single products, the type of which is commonly a function of the nature of the electrode;
- the use of a catalytic amount of a chemical oxidizing or reducing agent; this catalyst performs the oxidation or reduction of the organic substrate and is regenerated electrochemically after separation from the reaction products; these processes are called indirect (or mediated) electrolysis;
- an inherently pollution-free process; and
- the use of inexpensive raw materials.

Disadvantages of electroorganic synthesis include

- the cost of electricity,
- high capital costs,
- underdeveloped technological aspects, and
- complex and poorly understood reaction variables.

(See Baizer 1973; Fry 1972; Ross et al. 1975; Tomilov 1972; and Weinberg 1975.)

To the list of advantages one should add the fact that if suitable anodic and cathodic processes are selected, electroorganic syntheses can be used to make products at both anodes and cathodes in matched or paired syntheses (an example is the production of chlorine and caustic by the chloralkali industry). In addition, electrochemical syntheses are well suited to automation and thus require little manual labor.

To illustrate some of the advantages and the disadvantages of these processes, let us compare the chemical and the electrochemical routes to hydroquinone from benzene. Figure 1-1 is a simplified diagram of the chemical process, which involves the intermediate nitration of benzene followed by the chemical reduction of the nitro group to an amino group. The aniline thus formed is subsequently chemically oxidized to benzoquinone, which is finally reduced to the desired product, hydroquinone. Therefore, a four-step chemical process yields hydroquinone. Millington (1975) calculated the total energy requirement of the route as 70 MWh/metric ton of hydroquinone. Recent calculations by Beck et al. (Electrochemical Technology Corp. 1979) give about half of Millington's value using more modern technology. In the chemical process, the disposal of salt sludges and solutions is an important parameter when the environment is considered.

A simplified diagram of the electrochemical process is shown in Fig. 1-2. The electrochemical route is a one-step process in which benzoquinone is formed at the anode (possibly through the intermediate oxidation by HO• radicals) and subsequently reduced at the cathode to hydroquinone with the solvent reduction to hydrogen being the main competing cathodic process. If a divided cell is used, benzoquinone is pumped to the cathode compartment. This is an example of a paired synthesis, in which useful products are formed at both the cathode and anode.* The total energy usage calculated by Millington for this route is 44 MWh/metric ton of hydroquinone, in reasonable agreement with more recent

*This paired synthesis has been performed at a small pilot scale (Fremery et al. 1974). Variations using indirect electrolyses have also been described (Keidel 1975). The Electricity Council/Stavely Chemical Co. piloted the electrochemical oxidation of benzene to benzoquinone. The hydroquinone is obtained by chemical reduction with SO₂ (Electrochemical Technology Corp. 1979).

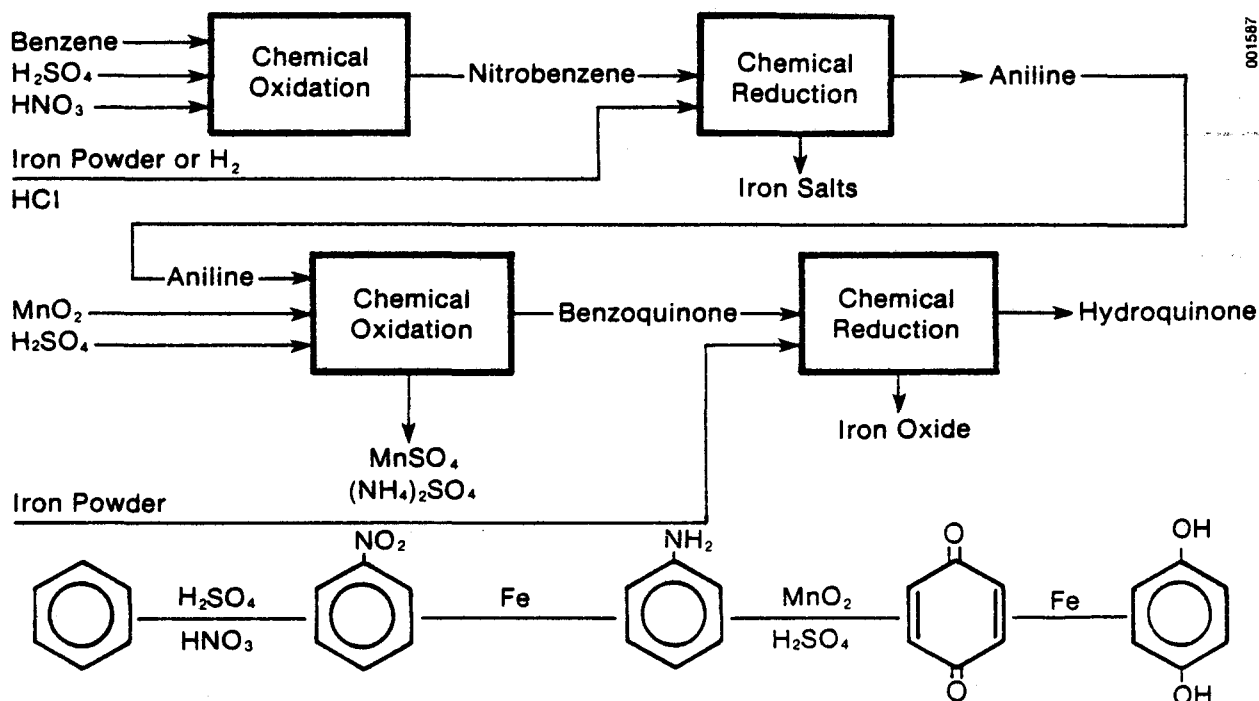


Figure 1-1. Simplified Chemical Synthesis Route from Benzene to Hydroquinone

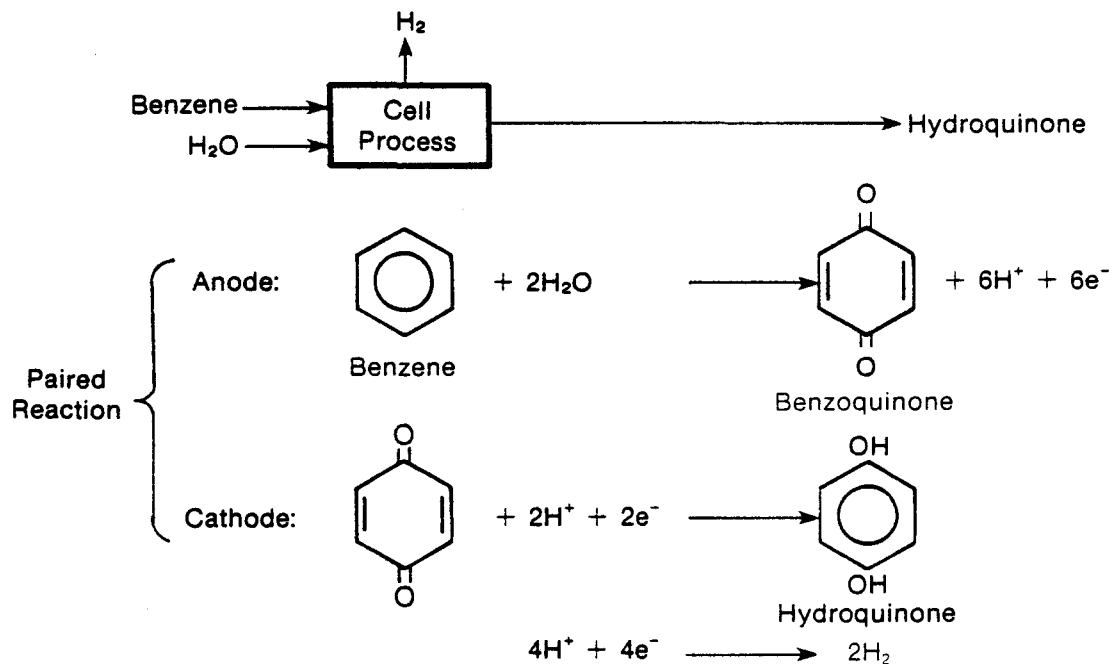


Figure 1-2. Schematic Diagram of Electrochemical Synthesis of Hydroquinone from Benzene



calculations by Beck et al. About 65% of this energy is used in the electrolytic process.

The electricity requirements of the electrolytic processes are

$$\text{power usage (kWh/kg)} = \frac{V \times F \times n}{M \times \text{CE}},$$

where

- V = cell voltage (V),
- F = Faraday constant = 96,500 C = 26.8 Ah = 1 mole of electrons,
- n = number of faradays used per mole of product formed,
- M = product molecular weight, and
- CE = current efficiency = fraction of the total current utilized for the production of the desired product.

For a given process, n and M are fixed, and therefore the only parameters that can be varied to promote energy economy are V and CE. The cell voltage is composed of

- the thermodynamic reversible cell potential;
- overvoltages at both anode and cathode needed to drive the reactions at a practical rate;
- the resistance drop (current \times resistance = IR) across the electrolyte for an undivided cell or the resistance drop across the catholyte plus anolyte for a divided cell; and
- the resistance of the separator in a divided cell.

Of these, only the thermodynamic potential cannot be decreased. Research on electrode materials and electrocatalysis can decrease the overvoltages; the IR drop can be decreased through better cell design. The proper cell design, electrodes, solvent and supporting electrolyte, and separator material can provide significant energy savings in an electrolytic process. An example is given by Millington (1975) in the benzoquinone synthesis in which the use of a capillary gap cell (Beck and Guthke 1969) can increase the current efficiency of the process two to three times.

Fitzjohn (1975) compared the investment for electroorganic versus non-electrolytic processes and demonstrated that the investments for the electroorganic processes were competitive for at least 70% of the chemical processes randomly selected. Though the calculations were performed in 1975, the capital investment increase between 1975 and 1981 should be roughly the same for both the electroorganic and chemical processes. In another recent study, Beck et al. (Electrochemical Technology Corp. 1979) compared electrolytic versus chemical processes for the synthesis of nine compounds. Power costs were not always the major fraction of the total cost in the electrochemical processes analyzed; separation of the products from their solvents was the energy-intensive step in many cases. As one would expect, there are cases where the electrochemical route is more energy efficient than the chemical catalytic processes (e.g., the adiponitrile synthesis), cases where the reverse situation is found, and cases where both processes are equally energy efficient. Electrochemical processes are more energy efficient when the product molecular

weight is high and the electrolysis step involves four or fewer faradays per mole of reactant. Additional savings in the electroorganic process are obtained if the raw materials (e.g., biomass-derived) are less expensive than those for the chemical routes.

Several papers in the literature deal with the industrial applications of organic electrosynthesis. Examples include Goodrich 1966; Fleischmann and Pletcher 1975; Clarke, Kuhn, and Okoh 1975; Fitzjohn 1975; and Baizer 1980. As pointed out by Beck et al. (Electrochemical Technology Corp. 1979):

The increased understanding of electroorganic reactions, the development of electrochemical engineering as a quantitative discipline to quantitatively design cells and processes, and the increasing awareness of electrochemical processing by chemical engineers will lead to more electroorganic processing.

1.3 ORGANIZATION

Section 2.0 reviews the electrochemistry of selected polysaccharides and monosaccharides, including cellulose, hemicelluloses, and starch. The electrochemistry of lignins and pyrolysis chars of lignins is reviewed in Section 3.0. In addition, due to the similarity of lignin chars to chars derived from coal and peat, the electrochemistry of these related compounds is described. Section 4.0 contains our conclusions and recommendations for further research in this area.

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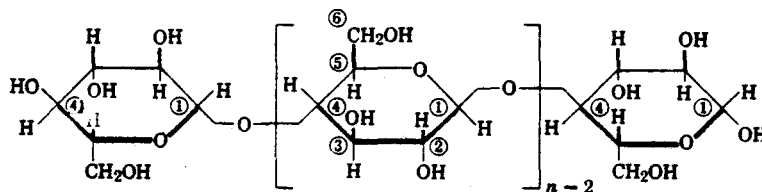
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SECTION 2.0

THE ELECTROCHEMISTRY OF SELECTED POLYSACCHARIDES AND MONOSACCHARIDES

Cellulose is the most abundant organic material on earth. It is a linear polymer of β -D-glucose, with the monomer units linked by 1,4-glycosidic bonds:



Cellulose

The number-average molecular weight varies from 10,000 (*in situ* in the wood) to 4000 (holocellulose) to 1500 (chemical pulps). The highly ordered crystalline structure limits the access of reagents and enzymes. The hydrolysis product is D-glucose (Goldstein 1980; Nikitin 1966). Cellulose is present in plant materials. About 50% of wood and 90% of cotton fibers are cellulose. The reader is referred to the excellent reference by Sjöstrom (1981) for a detailed review of the subject (Chapter 2).

Hemicelluloses are structural polysaccharides. They consist of several monosaccharides: for instance, pentoses (D-xylose, L-arabinose), D-hexoses [mannose, galactose, and glucose (to a small extent)], and smaller amounts of uronic acids and their derivatives and other methylated neutral sugars (see Fig. 2-1). The xylose-containing polysaccharide is commonly referred to as xylan. These polymers are usually branched and have a smaller degree of polymerization than cellulose. The hemicelluloses are species dependent. In woody plants, where hemicelluloses comprise roughly 25% of the cell wall, hardwoods are rich in xylan whereas softwoods are rich in mannose-containing polymers (galactogluco-mannans). Annual plants have a higher hemicellulose content and lower lignin content than woody species (see Section 3.0).

Starch, the reserve polysaccharide, is stored in the roots, seeds, tubers, stem pith, and fruits of plants (e.g., corn, wheat, rice, potatoes). Starch usually occurs as granules (2 to 150 μ m in diameter). It is composed of amylose and amylopectin. Like cellulose, starch is also a glucose polymer, but in starch the glycosidic linkage configuration is α . Linkages 1,4 and 1,6 occur in starches. Starches are composed of mixtures of two structurally different glucans. Hydrolysis of starch produces glucose.

Cellulose is very sensitive to oxidizing agents. The hydroxyl groups can be oxidized, forming ketones, aldehydes, or carboxylic acids. The extent of the degradation and the nature of the oxidized products depend on the nature of the oxidant and the conditions under which oxidation occurs. Nikitin (1966) and Sjöstrom (1981) review in detail the cellulose oxidation reactions.

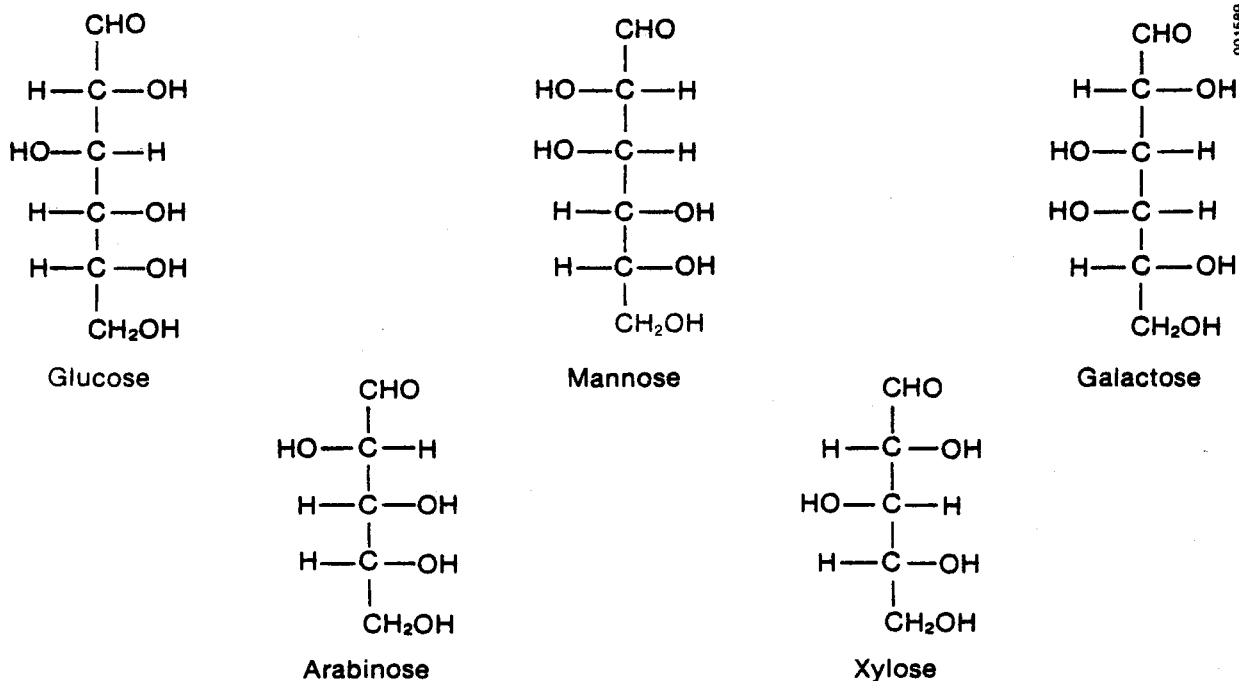


Figure 2-1. D-Aldoses in Acyclic Forms, Common Components of Carbohydrates Occurring in Nature

One of the most important oxidative degradation reactions is the autooxidation of cellulose by molecular oxygen in alkaline medium. This reaction is the basis of the "aging" of cellulose, through which the molecular weight of a number of cellulosic products such as rayon and cellophane can be adjusted to the required level. The reaction probably involves a hydroperoxide-type free-radical mechanism (e.g., Immergut 1975).

Periodates and lead tetraacetate are highly specific oxidants. These reagents attack the glycol at carbon positions 2 and 3. There is a simultaneous oxidation of the hydroxyl groups with cleavage of the C(2)-C(3) bond of the pyranose ring. The resulting oxidized cellulose is the dialdehyde cellulose and is obtained in high yields (>95%) (see, for instance, Hearon et al. 1978). A similar reaction occurs with starch, leading to dialdehyde starch. The dialdehydes can be employed as surface size and coating adhesives in the paper and paperboard industries.

Chlorine dioxide, chlorites, and chlorates oxidize the terminal hemiacetal groups of cellulose or aldehyde groups, formed by oxidation with other reagents (pH 3-5), to carboxyl groups. Chlorine dioxide does not react with the hydroxyl group of cellulose in acid medium. These oxidizing agents also oxidize the lignin fraction, thus promoting the bleaching of the cellulose fibers (see Section 3.0).

Partial oxidation reactions can involve the 6-position of the glucose monomers. The oxidation to the corresponding aldehydes or to the carboxylic acids can be observed. Nitrogen dioxide oxidizes mostly the primary hydroxyl groups to carboxyl groups.

Oxidative reactions are coupled to the hydrolysis of the glycosidic bonds. Aldonic acids (C-1 oxidation) can be formed, including the acids of the lower aldoses formed by fragmentation.

Reduction of aldoses by hydrogen on catalysts converts these sugars to polyhydroxy alcohols. Reduction of glucose in this manner leads to sorbitol, an effective bacteriostat and food additive.

In this report the electrolysis of these polymers is reviewed. In addition, the electrochemistry of some of the pertinent monosaccharides, principally glucose, is reported. Emphasis is given to the literature on syntheses. However, selected work on fuel cells for power generation using these compounds is also reviewed briefly.

2.1 THE ELECTROCHEMISTRY OF CELLULOSE, HEMICELLULOSES, AND STARCH

2.1.1 Synthetic Applications

In 1913, Oertel reported that by electrolysis on platinum electrodes of cotton suspended in neutral-pH solutions containing 16% potassium chloride, 60%-70% of the cellulose was dissolved, degraded, and oxidized to lower-molecular-weight entities. This was indicated by the large copper number--about 30--observed (the copper number reflects the number of total reducing groups on the cellulose, determined by reduction of the Fehling solution) (see Nikitin 1966, p. 77). By varying the electrolyte concentration, current density, and time, gel-gums were obtained which had adhesive properties (Choudhury and Khundkar 1952). The copper number and the total uronic carboxylic acid content increased with increasing electrolyte concentration and current density. The concentration of total carboxylic acids increased up to 8 hours and then decreased. The copper number increased steadily with the electrolysis time. There may be simultaneous hydrolysis of glycosidic bonds and oxidation of the -C-OH groups in the pyranose ring.

Cellulose electrolyses in acid medium [0.5 M H_2SO_4 , saturated $(NH_4)_2SO_4$] led to considerable degradation of cellulose (Choudhury and Khundkar 1953). The oxidized cellulose appeared to retain its physical strength and fibrous character. Increased copper numbers were obtained but the corresponding increase in carboxylic acid was not so pronounced.

Electrolysis of colloidal solutions of hemicelluloses was investigated as a means to recover the alkaline solution from a caustic waste liquor (5 M NaOH) from a viscose plant (Lenoble 1925, 1929). When 4.2 V were applied to the cell, the dissolved hemicelluloses (2% wt/wt) were oxidized to CO_2 and H_2O in an asbestos separated electrolysis cell. At the cathode, pure hydrogen was collected. At the anode, $Na_2CO_3 \cdot 10H_2O$ crystallized out of solution. Since the solubility of the hemicelluloses decreased with increased Na_2CO_3 content, toward the end of the electrolysis a small quantity of the polysaccharide precipitated out of solution.

Electrolysis of starch, collodion, gum arabic, etc. were preliminarily investigated in neutral solutions (Brester 1867). As expected, under the

experimental conditions, the electric current had very little effect on these polymers. Forty years later, Neuberg (1909) investigated the electrolysis of about 60 organic compounds, including starch, mannitol, and raffinose. Neuberg found that after many days the polymers (starch, dextrin) were fragmented into the constituent sugars, and these were degraded in a stepwise fashion to the lower sugars.

Farley and Hixon (1942) reported that cornstarch could be oxidized by alkaline electrolysis in a sodium chloride solution. The rigidity and gel strength of pastes from the oxidized starch decreased as the extent of oxidation increased.

One of the most successful electrolyses of these glucose polymeric materials was carried out in the 1960s. It was the indirect oxidation of starch to dialdehyde starch (Mehltretter and Wise 1969; Conway and Sohns 1959; Pfeifer et al. 1960; Lancaster et al. 1964). Initially, a cell was employed with a PbO_2 anode, a steel cathode, and a porous aluminum oxide separator. The anolyte was an aqueous sodium sulfate solution containing iodic acid. Figure 2-2 shows the reactions at the anode compartment. Later a two-stage process was devised in which the iodic acid was converted to periodic acid in the electrochemical cell, and this reactant was then pumped into a chemical reactor where starch was oxidized. This process was carried out at commercial scale but was terminated (see Weinberg 1979).

Fehér (1961) proposed and developed alternative methods using the Cr(VI)/Cr(III) couple as the oxidizing agent. Comparative kinetic studies of the chromium and the periodate/iodate couples were carried out. A pilot-scale demonstration was constructed using the proposed method.

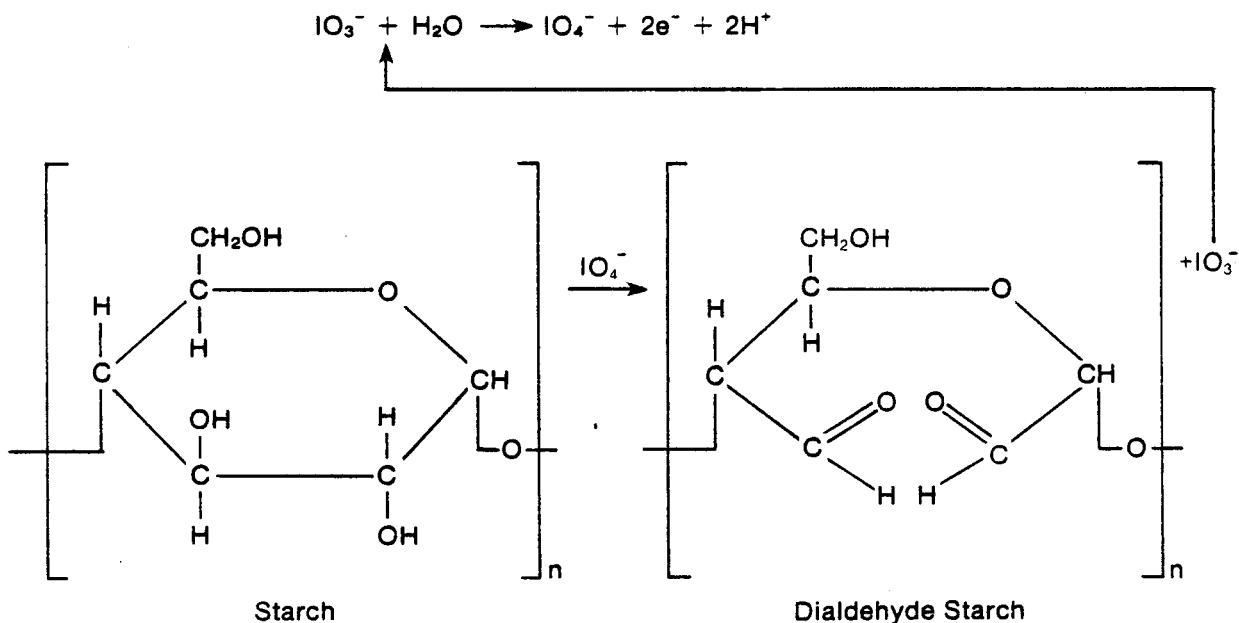


Figure 2-2. Indirect Oxidation of Starch to Dialdehyde Starch

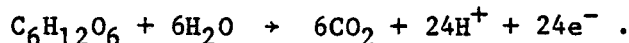
Both cellulose (Indira et al. 1975) and starch dialdehyde can be reduced electrochemically at mercury electrodes. Petropavlovski et al. (1977) used the polarographic analytic method for the kinetic investigations of starch oxidation by periodic acid.

2.1.2. Fuel Cell Applications

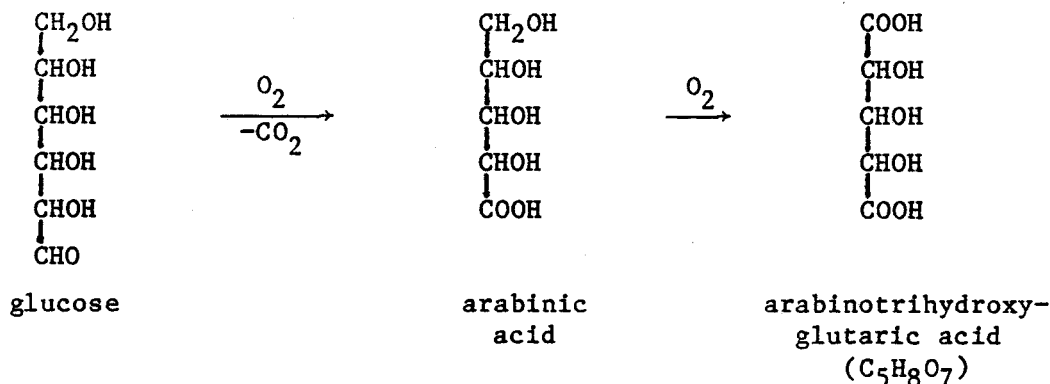
Bockris, Piersma, and Gileadi (1964) investigated the possibility of using cellulose and starch as fuels for fuel cell systems. For comparison, simpler carbohydrates such as sucrose, cellobiose (β -D-glucose dimer), and glucose were investigated under the same experimental conditions. The media employed were 40% H_3PO_4 and 5 N NaOH, at temperatures of 80°-100°C. A platinized platinum gauze electrode (52 cm²) was used as the anode.

Figure 2-3 compares the rates for anodic oxidation of the various carbohydrates investigated in alkaline medium at 80°C. As expected, the reactivity decreases as the complexity of the molecules increases. From the activation energies (~10 kcal/mol for cellulose) one would expect current densities of ~5 mA/cm² at higher temperatures, which can be obtained in alkaline solutions.

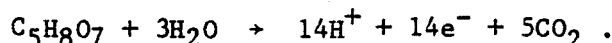
Bockris et al. (1964) found experimentally that 2 F were involved in the evolution of a mole of CO_2 . For simplicity, the stoichiometric equation is written for the monomer, glucose:



According to this equation, 4 F are involved in the production of a mole of CO_2 . The discrepancy between experimental results and the stoichiometric equation was explained by postulating that chemical oxidation reactions are coupled with the degradation of the glucose unit (see Section 2.2.1):



and



According to this scheme, 2.3 F would be used per mole of CO_2 evolved, which agrees well with experimental results. The contribution of the chemical reaction to CO_2 evolution in this scheme agrees with blank tests with no

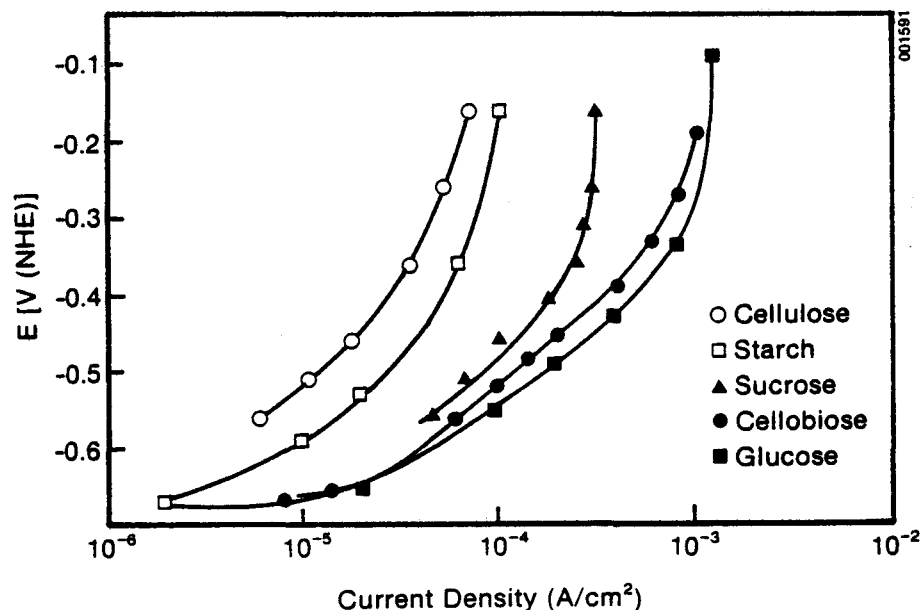


Figure 2-3. Comparison of the Rates for Anodic Oxidation of Various Carbohydrates in NaOH at 80°C. From Bockris et al. 1964.

current (~15% of the amount obtained during anodic oxidation) (Bockris et al. 1964).

Measurements at 120°C indicated that a power density of ~1 mW/cm² could be obtained in a cellulose-air fuel cell. These results suggested electrochemical oxidation and degradation of cellulose as a possible way to treat cellulosic waste in space vehicles.

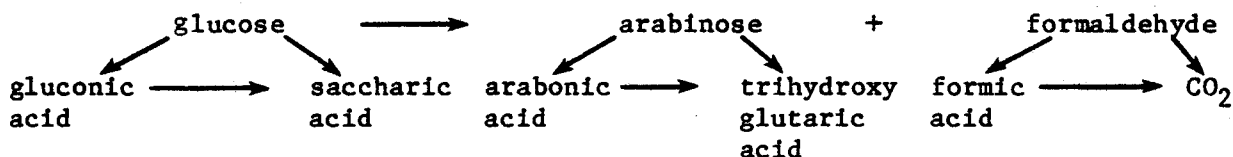
2.2 THE ELECTROCHEMISTRY OF SELECTED MONOSACCHARIDES

The electrochemistry of monosaccharides and derived compounds has been thoroughly reviewed by Fedoronko (1974), who emphasizes the use of polarographic techniques for carbohydrate analysis and covers the homogeneous reactions taking place (such as ring-opening of the cyclic hemiacetal to the aldehydic form before the electron transfer processes) that are valuable for understanding carbohydrate chemistry as well as for carbohydrate analysis. Due to the wealth of literature in this area and the recent, very comprehensive review article, these aspects of the electrochemistry of monosaccharides are not described in our report. Fedoronko's review also covers in detail the synthesis of aldonic acid and polyhydric compounds. Therefore, we present only a summary of the relevant synthesis work and the most recent literature.

2.2.1 Oxidative Degradation

It has long been known that acidic solutions of glucose can be oxidized and degraded. Systematic investigations by Loeb (1909, 1910) and Neuberg (1908,

1909) show that the electrolysis products undergo oxidation and fragmentation followed by oxidation. On PbO_2 anodes in sulfuric acid solutions, oxidation products are gluconic acid $[\text{CH}_2\text{OH}(\text{CHOH})_4\text{COOH}]$ and saccharic acid $[\text{COOH}(\text{CHOH})_4\text{COOH}]$, as well as compounds resulting from fragmentation followed by oxidation, such as arabinic acid $[\text{CH}_2\text{OH}(\text{CHOH})_3\text{COOH}]$, trihydroxyglutaric acid $[\text{COOH}(\text{CHOH})_3\text{COOH}]$, and formaldehyde, formic acid, and CO_2 :



Neuberg et al. (1910) verified that carbon dioxide could be electrolytically split from the aldonic acids, with the formation of the lower aldoses. The mechanism proposed for the oxidation was the formation of aldonic acid and 2-ketoaldonic acid, which decarboxylate into the lower aldoses. The degradation cycle would be repeated until the conversion of the monosaccharide into carbon dioxide was complete.

Similar oxidation and degradation of D-glucose, D-mannose, methyl- α -D-glucopyranose, D-glucono-1,5-lactone, D-galacturonic acid, and maltose were observed in alkaline methanol or ethanol (sodium or potassium alkoxide) on graphite electrodes. All the possible lower aldoses and formaldehyde were detected by paper chromatography (Hay and Smith 1969).

Under controlled conditions, the electrolysis of the aldonic acids can be restricted to synthesis of the aldosulonic (α -ketoaldonic) acids or the lower aldoses (see Fedoronko 1974).

Table 2-1 summarizes the electrolytic oxidation products for selected compounds.

2.2.2 Syntheses of Aldonic Acids and Related Substances

The synthesis of aldonic acids from the corresponding aldoses is an example of successful indirect electrolyses. It was developed in the 1930s by Isbell and Frush. This synthesis consists of the electrochemical oxidation of bromide ions to bromine (in equilibrium with hypobromite) (Podesta et al. 1974) or to hypobromite (Fioshin et al. 1969; Avrutskaya and Fioshin 1969). Fast chemical reactions follow the discharge of bromide ions. The hypobromite ions chemically oxidize the glucose (or other saccharides; see Table 2-2) to gluconate ions and regenerate the bromide ions, which are recycled. Therefore, a small amount of bromide ions can oxidize a large amount of carbohydrate. The pH of the medium is kept reasonably constant at ~ 6.2 by carrying out the reaction in the presence of calcium carbonate or other alkaline-earth metal carbonates. At this pH the further oxidation of gluconic acid into saccharic acid is minimized (Fink and Summers 1938). Current inefficiencies are due to small contributions of the further oxidation of hypobromite to bromate ions (Fioshin et al. 1969). The cathodic reaction is the sacrificial reduction of the solvent water to hydrogen. Rotating electrode kinetics (Sathyanarayana and Udupa 1958; Udupa and Dey 1956) and alternating current electrolyses

Table 2-1. Electrolytic Oxidation and Degradation Reactions of Selected Monosaccharides and Derived Compounds

Compound	Medium	Electrode	Product(s)
Glucose	5% H ₂ SO ₄	PbO ₂	gluconic, saccharic, arabonic, trihydroxyglutaric, formic acids; formaldehyde; CO ₂
α -Methyl glucoside ^a	H ₂ O, H ₂ SO ₄ , Na ₂ SO ₄ , O ₂	Hg	glucuronic acid (20% yield)
2,3:4,6-Di-O-isopropylidene-L-sorbose	NaBr, NiCl ₂ , pH 9.8	Cu, Ni, Ag monel	di-O-isopropylidene-L-xylohexulosonic acid (70%-90% yield)
Lactose ^b	H ₂ O, CaCO ₃ , Br ⁻	C	calcium gluconate, calcium oxalate, D-xylo-5-hexulose, calcium lactobionate
D-Idonic acid	H ₂ O, acetic acid, NaBr, CrO ₃	C	ketoidonic acid, or D-xylohexulosonic acid
D-Gluconic acid or calcium gluconate	H ₂ O, acetic acid, CaBr ₂ , CrO ₃	C	calcium 2-ketogluconate (80% yield)
Calcium 2-keto gluconate	H ₂ O, CaBr ₂ , acid	C	calcium D-arabonate
L-Arabonic acid	H ₂ O	Pt	L-erythrose
D-Gluconic acid	H ₂ O	Pt	D-arabinose

Source: Fedoronko 1974, Weinberg and Weinberg 1968, and references therein.

^aCathodic oxidation by electrochemically generated hydrogen peroxide.

^bOxidation with more than 2 F/mol reactant.

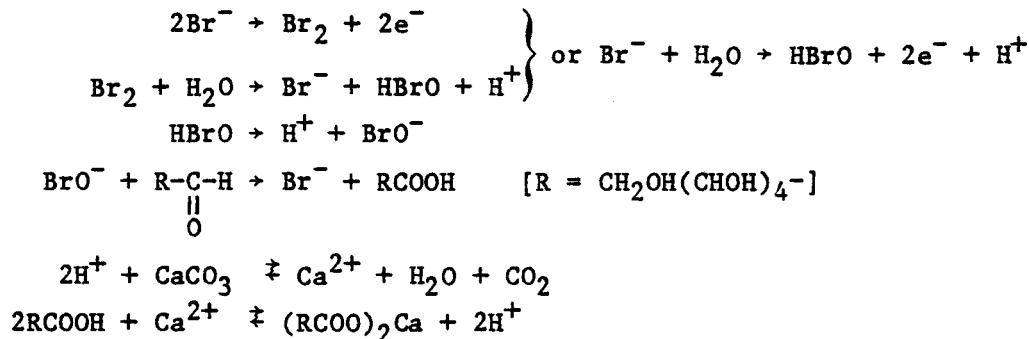
Table 2-2. Electrolytic Oxidation Reactions of Selected Saccharides to the Corresponding Salts

Compound	Medium	Electrode	Product(s)
Glucose	H ₂ O, NaBr	C, Fe, Ni	calcium gluconate (85%-100% yield)
	CaCO ₃	C, Cu, Pb	calcium 5-ketogluconate (10% yield)
D-Galactose	H ₂ O, KBr, CaCO ₃	C	calcium galactonate (60%-70% yield)
3-Methylglucose	H ₂ O, CaBr ₂ , CaCO ₃	Pt	calcium 3-methylgluconate (100% yield)
D-Mannose	H ₂ O, CaBr ₂ , CaCO ₃	C	calcium mannonate (92% yield)
D-Xylose	H ₂ O, CaBr ₂ , CaCO ₃ , Br ₂	C	cadmium xylonate (65% yield)
	H ₂ O, Br ⁻ , MgCO ₃	C	magnesium xylonate (80% yield)
	H ₂ O, NaBr, or SrCO ₃	C	strontium xylonate (95% yield)
D-Maltose	H ₂ O, KBr, CaCO ₃	C	calcium maltobionate (75% yield)
D-Lactose	H ₂ O, KBr, CaCO ₃	C	calcium lactobionate (70%-90% yield)
Arabinose	H ₂ O, CaBr ₂ , CaCO ₃	Pt	calcium arabinatate (65%-70% yield)

Source: Fedoronko 1974, Weinberg and Weinberg 1968; and references therein.

(Kappanna and Joshi 1952) have also been investigated. High current densities and low frequencies favor the process.

The following are the proposed reactions occurring during the synthesis:



The following references contain descriptions of the patented procedures for the syntheses of aldonic acids: Isbell 1934, 1936; Helwig 1933; Rohm and Haas Co. 1931, 1932.

Calcium gluconate synthesis appears to be practiced commercially by Sandoz-Chefaro (see Electrochemical Technology Corp. 1979). In addition, in India small-scale electrolytic production of calcium gluconate is presently practiced using rotating graphite electrode cells. The cell voltage is 10 to 12 V, operating at 10-15 A/dm², with a consumption of electricity of 4 kWh/kg (Udupa 1979).

The mechanism of the direct anodic oxidation of glucose in 1 M H₂SO₄ on platinum electrodes has been investigated (Skou 1977). Glucose adsorption on the electrode is an equilibrium reaction and follows a Langmuir isotherm. The adsorbed glucose rearranges to the corresponding enediol, which can diffuse into the bulk of the solution or becomes oxidized in a two-electron process to gluconic acid (Skou 1977). Ernst et al. (1979) have also investigated the electrode mechanism of this electrooxidation at pH 7.5 (phosphate buffer). These authors suggest that the hemiacetal group is the reactive center and that there is adsorption of glucose and/or products. The primary oxidation product is the gluconolactone.

2.2.3 Syntheses of Polyalcohols

The literature on the electrochemical reduction of monosaccharides is comprehensively reviewed by Fedoronko (1974). Another excellent review of the literature and investigations of electrode materials for the reduction of glucose, fructose, and mannose is given by Parker and Swann (1947).

The preparative electroreduction of D-glucose has been extensively investigated. In aqueous solutions, this carbohydrate is present in the cyclic hemiacetal form, and the ring opens to the aldehydic form in an acid/base-catalyzed reaction. The aldehydic form is the electroactive species. Therefore, a basic medium will increase the rate of electroreduction. However, a

strong basic medium also favors the isomerization of D-glucose into D-mannose and D-fructose, with simultaneous dealdolization and dehydration. A summary of possible reactions occurring in the electrolysis in alkaline medium is shown in Fig. 2-4. Sorbitol and mannitol are the main reduction products, but the other products shown have also been isolated and characterized (see Fedoronko 1974).

The conditions for the electrolytic production of sorbitol and mannitol were initially proposed by Creighton (1926, 1927, 1939, 1943). The Atlas Powder Co. began production of 1500 t/yr in 1937, as described by Killeffer (1937) and Taylor (1937). However, in 1948 the process was replaced by catalytic hydrogenation. A recent survey (Electrochemical Technology Corp. 1979) indicates that chemical catalytic hydrogenation consumes about 10 times less energy than the electrochemical process, though the latter has not been operated in a continuous fashion or enjoyed the benefit of the recently developed cell designs or pairing to another process, e.g., glucose oxidation to gluconic acid.

Smirnova et al. (1973) report tests of 20 cathode metals and some of their alloys for the reduction of glucose to sorbitol. Cathodes with high overvoltage and high surface catalytic activity, such as Hg, Pb, Zn, Zn/Hg, Pb/Cu, and Sn/Hg, gave 40%-70% of the current efficiency of the polyalcohol. Most of these findings agree with those of Parker and Swann (1947).

There is also mention in the patent literature of the possibility of improving the electrolytic process by using an anion exchange membrane as a separator in H_2SO_4 medium. The anodic reaction would provide the acid to be used in the cathodic side and favor the separation. However, no details of compounds or conditions are given in the patent description (Societe Sorapec 1976).

Table 2-3 summarizes the polyalcohols that have been prepared, as a function of the medium and the nature of the electrode.

2.2.4 Fuel Cell Applications

In the 1960s several companies carried out screening programs on the activity of organic fuels, including glucose, in direct organic fuel/oxygen fuel cells. For instance, Monsanto Research Corp. (1962) screened 148 compounds. Half-molar solutions or suspensions of the fuel were tested in basic (1 M KOH, $pH \approx 14$), acidic (1 M H_3PO_4 , $pH \approx 1$), and neutral (KOH- H_3PO_4 buffer, $pH \approx 7$) solutions at 30° and 90°C. Platinized platinum and platinized porous carbon electrodes were tested. Current-voltage curves were obtained by scanning from 0 to 100 mA/cm². Figure 2-5 reproduces such data for glucose. The results were reproducible within about 20%. The preparation of the electrodes was believed to be the source of irreproducibility. Table 2-4 lists the current densities for various fuels at 0.5 V versus the hydrogen electrode on platinized platinum electrodes. Underlined are the biomass-derivable organic fuels tested (cf. Fig. 2-1).

California Research Corporation (CRC) (1962) tested 43 organic fuels in basic electrolyte between 25° and 80°C. Table 2-5 lists in the order of decreasing activity the 19 fuels tested in alkaline media by both Monsanto and CRC on platinized carbon electrodes.

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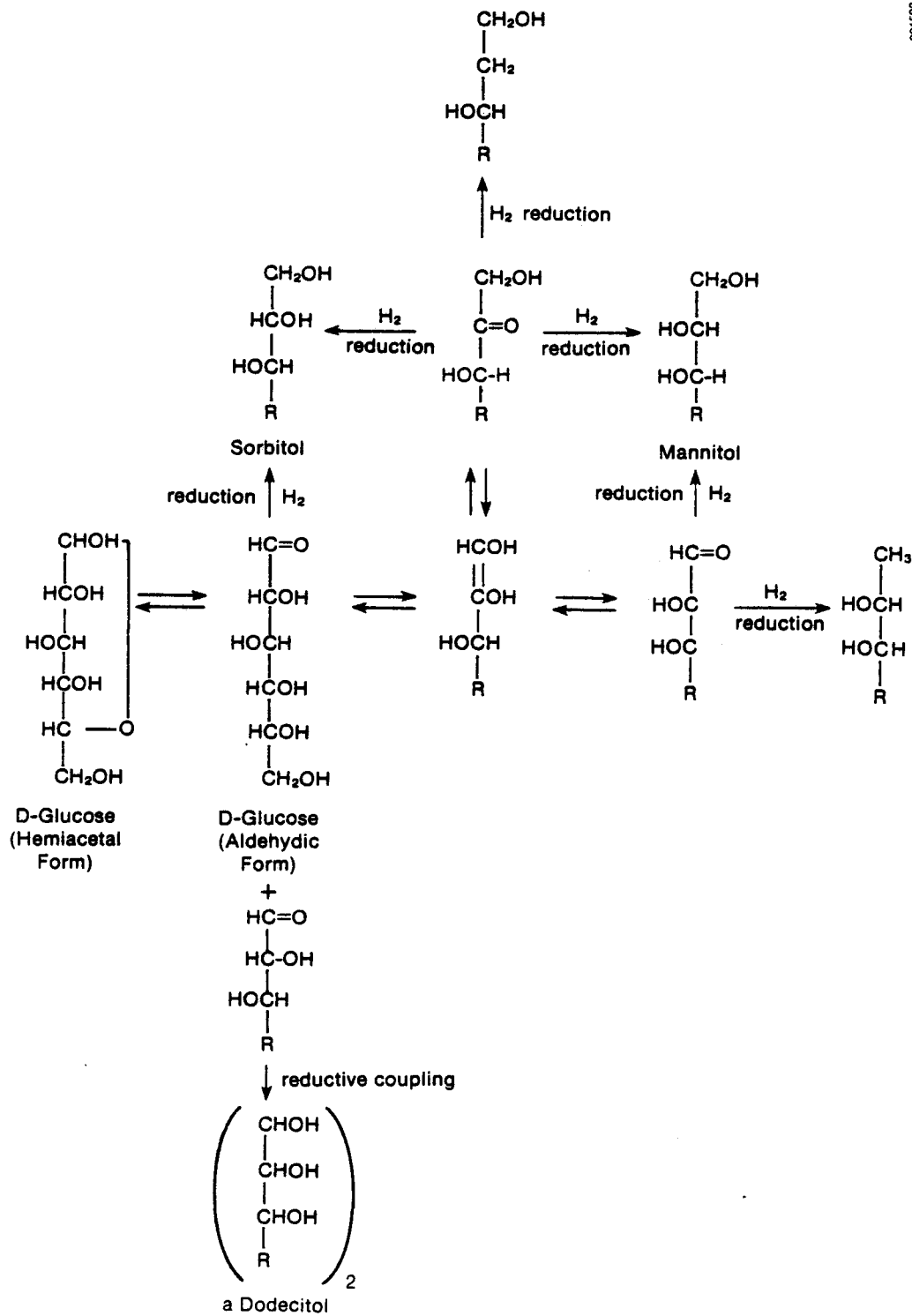


Figure 2-4. Electroreduction Reactions of Glucose

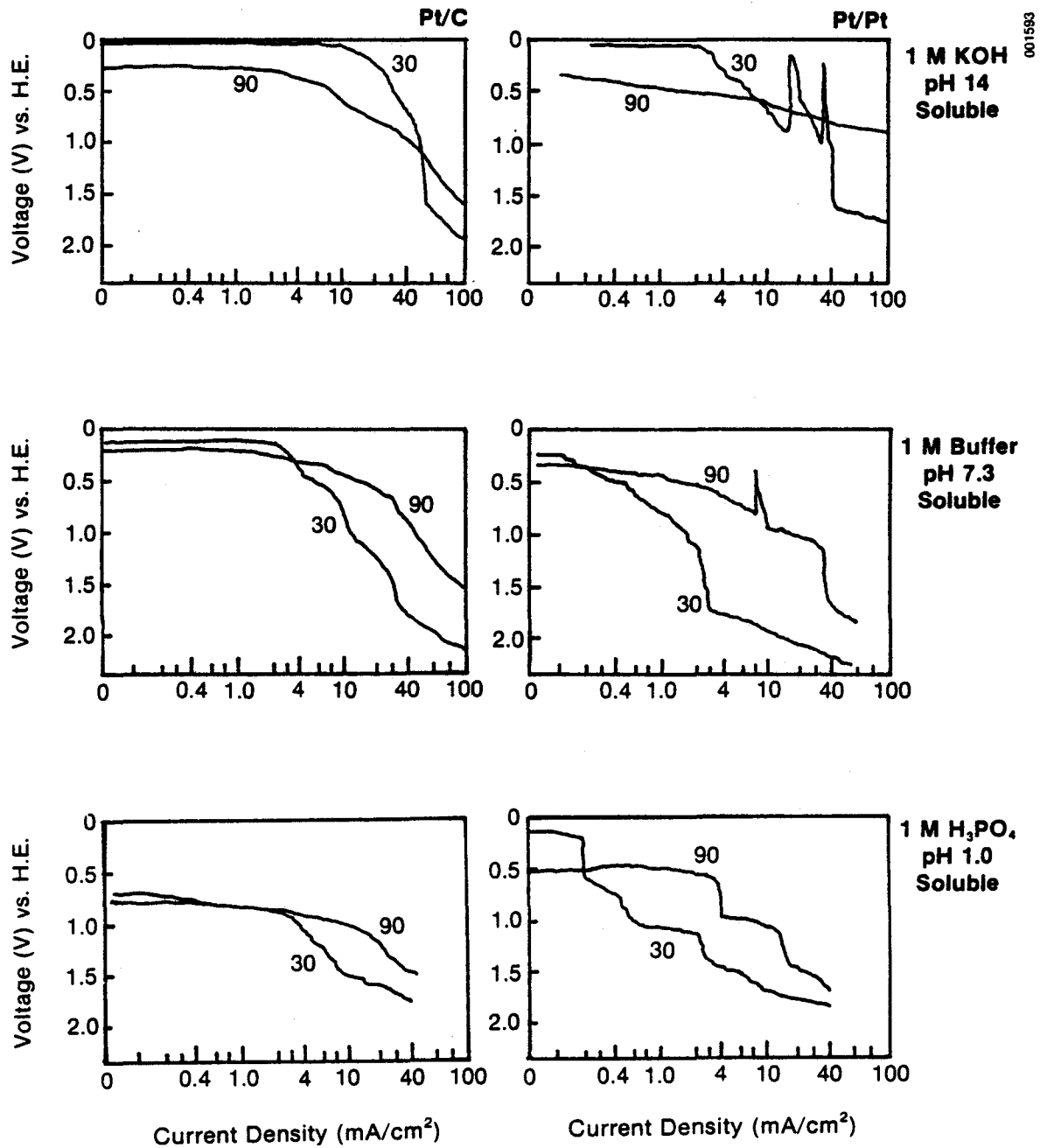


Table 2-3. Electrolytic Reduction of Certain Saccharides at 30°C

Compound	Medium	Electrode	Product(s)
Glucose	0.5 N NaOH	Pb/Hg	sorbitol, 60%-70% yield mannitol, 15%-20% yield
Glucose	Na ₂ SO ₄ , ZnSO ₄ ^a	Zn/Hg or Pb/Hg	sorbitol, 82%-85% yield
Glucose	0.5 N NaOH	Pb	sorbitol, 45%-60% yield mannitol, 0%-10% yield
Mannose	0.5 N NaOH	Pb/Hg	mannitol, 65%-90% yield sorbitol, 0% yield
Mannose	0.5 N NaOH	Pb	mannitol, 88%-94% yield sorbitol, 0% yield
Fructose	0.5 N NaOH	Pg/Hg	sorbitol, 6%-16% yield mannitol, 20%-36% yield

SOURCE: Parker and Swann 1947; Fedoronko 1974; Popp and Schultz 1962; and references therein.

^a~0.05 N NaOH; catholyte pH between 1.5 and 7.

These preliminary investigations did not screen special electrocatalysts, as was done for the direct methanol fuel cell at that time (see Austin 1967 for a review of these activities). It was suggested that efforts should be made to investigate the behavior of these fuels at higher temperatures.

Parallel research activities related to glucose fuel cells started in the 1960s in the area of fuel cells for biomedical applications (range of milliwatts to watts): e.g., implantable pacemakers and glucose sensors for diabetes therapy. One example of the direct fuel cell approach involves a glucose-selective permeable membrane/ a porous glucose electrode/ an electrolyte matrix/ a porous oxygen electrode/ an oxygen-selective permeable membrane (Giner and Holleck 1972). Other approaches using selective membranes and the literature on the direct glucose fuel cell for pacemaker power are reviewed by Yao et al. (1972). Molybdenum dioxide salts derived from 4,4',4'',4'''-tetrasulfophthalocyanine were shown to act as catalysts at room temperature in neutral medium (Arzoumanidis and O'Connell 1969).

The more recent literature on this subject includes Gough et al. 1978, Colton et al. 1979, Lerner et al. 1979, and Marincic et al. 1979. See also Skou 1977.

Table 2-4. Current Densities for Various Fuels at 0.5 V vs. Hydrogen Electrode on Platinized Electrodes in Three Media

Current density (mA/cm ²)	1 M KOH		1 M Buffer		1 M	
	Temp. (°C)	Fuel	Temp. (°C)	Fuel	Temp. (°C)	Fuel
>100	90	hydrazine	90	formic acid (pH 6.1)		
	30	hydrazine				
	90	formohydrazide				
	90	semicarbazide-HCl				
50-100	30	formaldehyde	90	hydrazine (pH 9)	90	formamide
	30	formohydrazide	90	semicarbazide-HCl	90	hydrazine (pH 2.2)
	30	semicarbazide-HCl				
10-50	90	<u>methanol</u>	90	formaldehyde	90	<u>formic acid</u>
	90	<u>ethanol</u>	30	<u>formic acid</u> (pH 6.1)	90	<u>ethyl formate</u>
	30	<u>ethanol</u>	90	ethyl formate	30	hydrazine (pH 2.2)
	90	benzyl alcohol	90	formamide	90	formohydrazide (pH 1.6)
	90	ethylene glycol	30	hydrazine (pH 9)	90	semicarbazide-HCl
	90	1,2-propanediol	30	semicarbazide-HCl	30	semicarbazide-HCl
	90	<u>glycerol</u>	90	thioglycolic acid (pH 5.9)	90	thioglycolic acid
	90	inositol			90	thiourea
	30	inositol				
	90	formaldehyde				
	90	5-hydroxypentanal				
	30	<u>glyoxylic acid</u> (pH 13.2)				
	90	diethyl oxalate				
	90	formamide				
	90	ethylene oxide				
	90	thioacetic acid (pH 13.2)				
	5-10	90	<u>isopropanol</u>	90	<u>methanol</u>	90
30		<u>isopropanol</u>	90	<u>isopropanol</u>	30	<u>ethanol</u>
30		<u>glycerol</u>	90	glyoxal	90	isopropanol
90		2-ethoxyethanol	90	formohydrazide	30	hydroquinone
90		diethylene glycol	90	ethylene oxide	30	<u>formic acid</u>
90		glyoxal (pH 13)	90	thioacetic acid (pH 5.8)	90	<u>glyoxylic acid</u>
30		<u>glucose</u>	30	thioacetic acid	30	ethyl formate
90		acetoin			90	hexamethylene-etraamine
90		methyl glyoxal			90	glycol formal
90		ethyl formate				
30		diethyl oxalate				
30		ethylene oxide				

Source: Gentile et al. 1962.

Note: Underlines indicate the organic fuels that can be derived from biomass.

Table 2-5. Relative Activity of Organic Fuels in Aqueous Alkaline Medium with Platinized Carbon Electrodes

Source	
Monsanto Research Corporation (1962)	California Research Corporation (1962)
hydrazine	hydrazine
formaldehyde	formaldehyde
<u>methanol</u>	<u>ethanol</u>
ethylene glycol	aminoethanol
<u>glycerol</u>	isopropanol
aminoethanol	ethylene glycol
<u>ethanol</u>	<u>methanol</u>
<u>glucose</u>	<u>glycerol</u>
<u>formic acid</u>	<u>glucose</u>
<u>isopropanol</u>	<u>formic acid</u>
<u>glycolic acid</u>	<u>glycolic acid</u>
allyl alcohol	allyl alcohol
<u>acetone</u>	<u>acetone</u>
<u>acetic acid</u>	t-butyl alcohol
maleic acid	<u>acetic acid</u>
dioxane	maleic acid
t-butyl alcohol	<u>oxalic acid</u>
<u>oxalic acid</u>	dioxane

Note: Fuels are listed in order of decreasing activity. Underlines indicate the organic fuels that can be derived from biomass.

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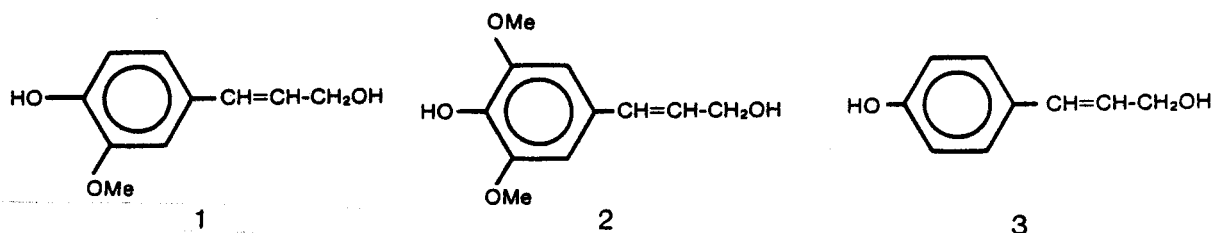
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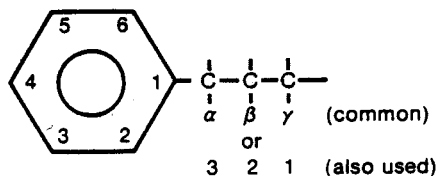
SECTION 3.0

THE ELECTROCHEMISTRY OF LIGNINS, PYROLYSIS CHARs OF LIGNINS,
AND RELATED COMPOUNDS

Lignins are complex irregular natural polymers that are present in plant materials in varying amounts depending on the species [including species of gymnosperm (softwoods); dicotyledonous angiosperm (hardwoods); monocotyledonous angiosperm]. These polyphenolic products arise from an enzyme-initiated dehydrogenative polymerization of three primary precursors: (1) transconiferyl (or 4-hydroxy-3-methoxycinnamyl), (2) transsinapyl (or 4-hydroxy-3,5-dimethoxycinnamyl), and (3) trans-p-coumaryl (or 4-hydroxycinnamyl) alcohols (Sarkanen and Ludwig 1971a):



Nomenclature:



Sarkanen and Ludwig (1971b), Nikitin (1966), and Sjöström (1981) describe in detail the determination of the structural elements of these polymeric materials, based on the chemical reactivity of these polyphenolic compounds, [mainly from the pioneering work by Freudenberg and Adler (e.g., 1977)]. Figure 3-1 shows a schematic formula for spruce wood lignin by Freudenberg with modifications by Harkin (1967).

Figure 3-2 shows the structure of beech lignin proposed by Nimz (1974). The major bond types in beech lignin and their proportions are listed in Table 3-1. These results show acyclic α - and β -ethers (mostly β -O-4) linkages to be the major type of bond in beech lignin. Most of the bonds linking monomeric units in lignins, β -O-4 and C-C (biphenyl or alkyl-aryl types), have extraordinary stability, both kinetic and thermodynamic. (The α -O-4 ether linkages are not as stable.) Therefore, degradation of these structures, e.g., by hydrolysis, is difficult. In addition, because units with reactive residues (e.g., benzyl alcohol, aldehydes) are present, secondary condensation reactions compete with hydrolytic processes. The extent of self-association reactions and/or hydrolysis is highly dependent on the medium and conditions employed, as well as on the species chosen (Sarkanen and Ludwig 1971b; Nikitin 1966).

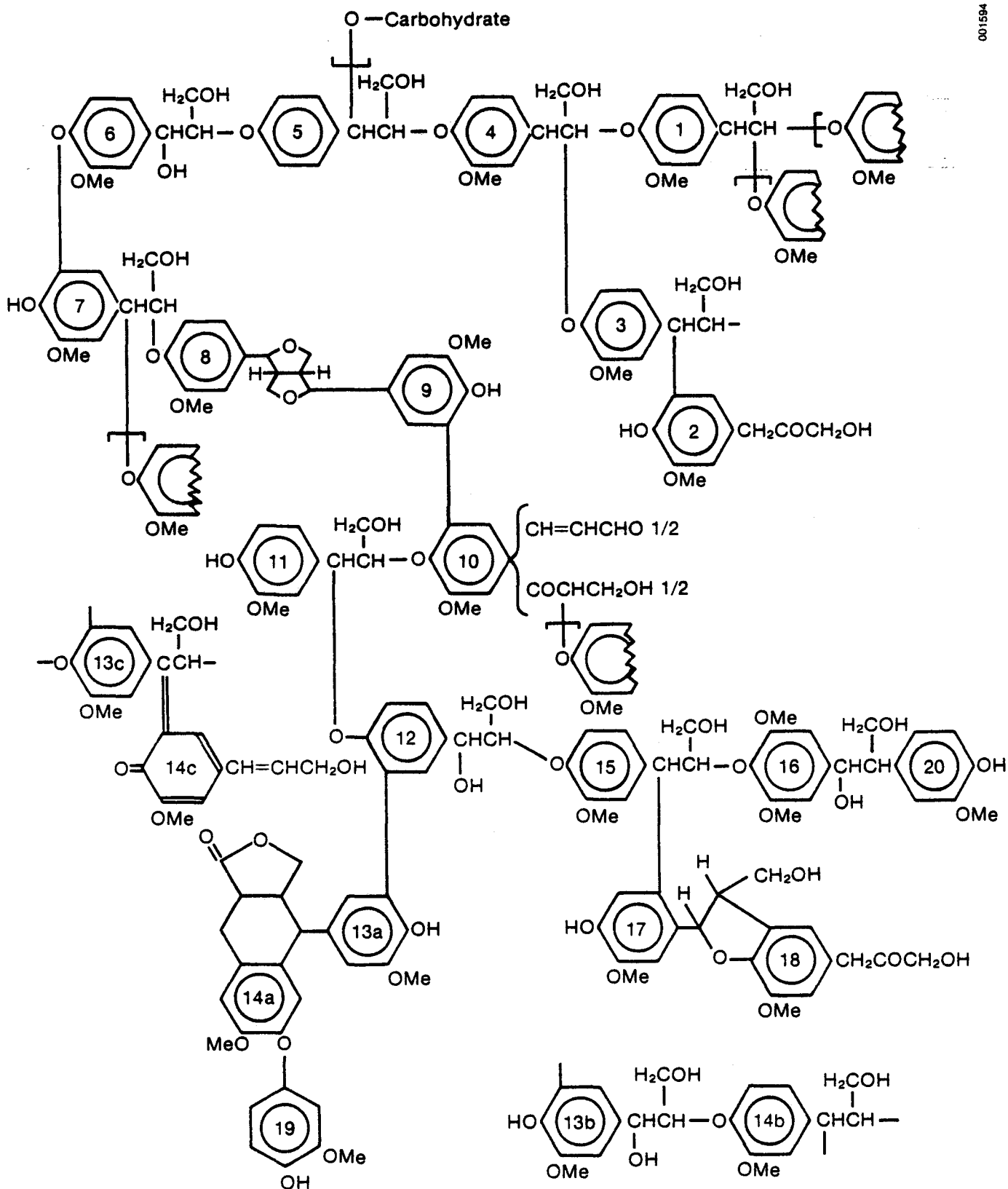


Figure 3-1. Schematic Formula for Spruce Wood Lignin. By Freudenberg (1965) with modifications by Harkin (1967).

Table 3-1. Proportions of Bond Types in Beech Lignin

Bond Type	Proportion (%)
Acyclic α - and β -ethers	65
β -1 bonds (1,2-diarylpropane units)	15
β -5 bonds (phenylcoumaran units)	6
β - β bonds (syringaresinol and pinosresinol units)	5
α - β bonds	2.5
5-5 bonds (biphenyl units)	2.3
β - β bonds in dibenzyltetrahydrofuran units	2
5-O-4 bonds (diphenyl ether units)	1.5
β - β and α -6 bonds (tetralin units)	0.5

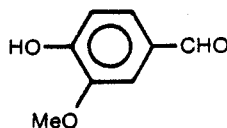
Source: Nimz 1974.

The lignins on the cell walls seem to be normally chemically bonded to the hemicelluloses. Most lignins also contain varying amounts of certain aromatic carboxylic acids in ester-like combinations. Lignins can be separated from the lignocellulosic material by a variety of pretreatments (Allen et al. 1980). Because the chemical reactions include self-association reactions, the structures of the lignins are modified according to the pretreatment used (e.g., hydrolysis, oxidation, organic solvents, milling) and are species dependent.

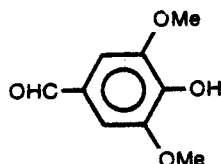
Lignins are more readily oxidizable than cellulose and other polysaccharides (see Section 2.0). They reduce Fehling's solution. The reducing capacity of the lignins depends on the method of isolation. The ease of lignin oxidation is used in pulping by the hydrogen peroxide and/or chlorine methods and in bleaching of the sulfite pulps by solutions of hypochlorites, chlorite, or chlorine. Investigations of the controlled oxidation of lignins in several media have helped to establish the aromatic nature of this polymer and to further the understanding of its complex reactivity (Nikitin 1966; Sjöstrom 1981).

Extensive oxidation of lignins by ozone or hydrogen peroxide in neutral or acetic acid media yields carbon dioxide, formic (~5%) and acetic (7%-10%) acids, and smaller amounts of dicarboxylic acids such as malonic acid ($\text{HOOC-CH}_2\text{-COOH}$), succinic acid [$\text{HOOC-(CH}_2\text{)}_2\text{COOH}$], and oxalic acid (HOOC-COOH). More drastic oxidation, e.g., by nitric acid, can give 20% oxalic acid. Alkaline autooxidation of lignins at ~200°C under pressure can yield not only fatty acids but also small amounts of aromatic acids; e.g., benzoic and phthalic acids (Nikitin 1966; Sarkanen 1975).

Mild oxidation of lignin by nitrobenzene at 160°C in alkaline medium yields vanillin



(~25% for softwoods) or vanillin and syringaldehyde

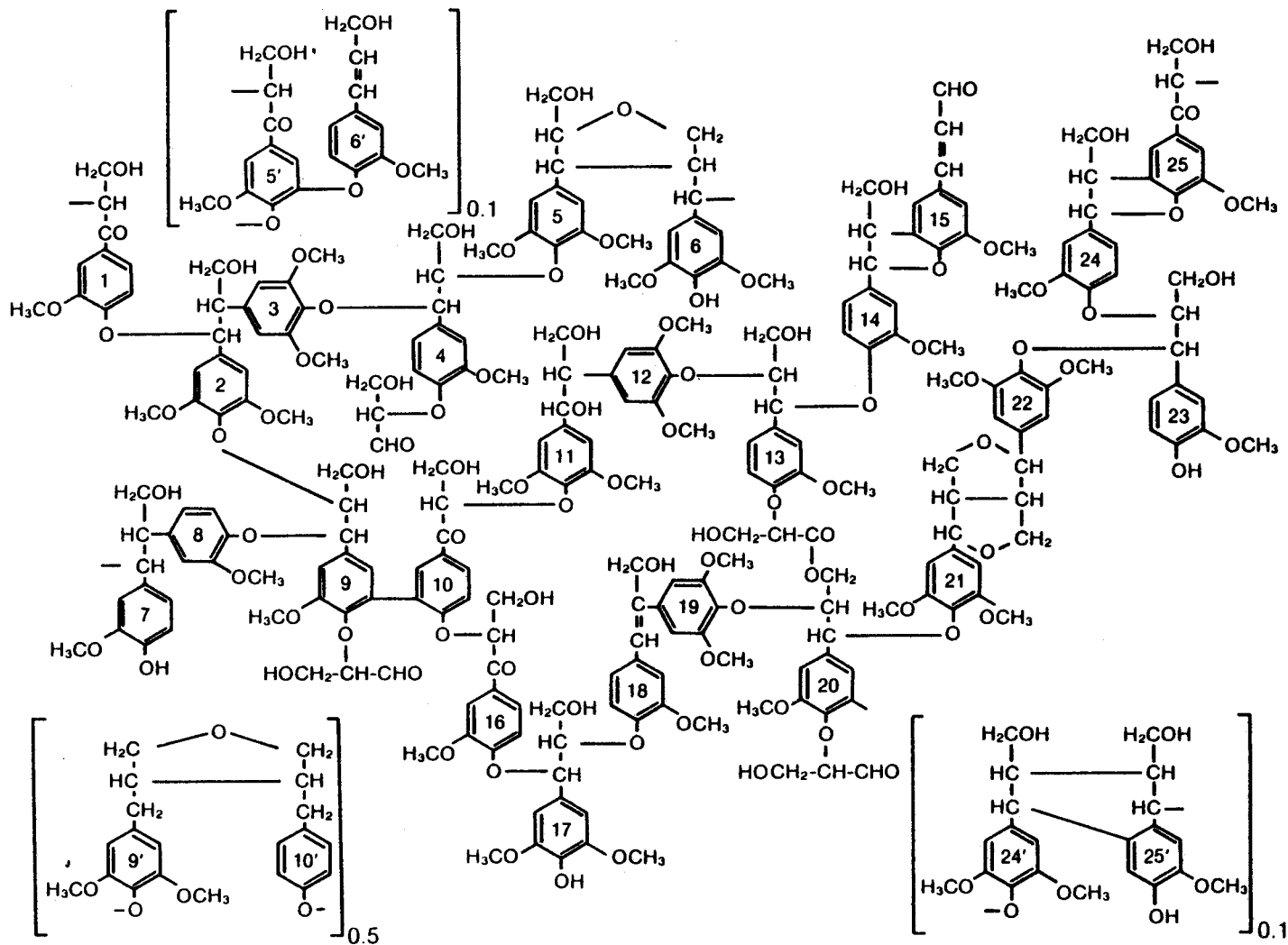


(up to 50% for hardwoods) (see Nikitin 1966). Vanillin is used in perfume, flavoring, and pharmaceutical products ($\sim 3 \times 10^6$ kg/yr). It is commercially produced by autooxidation of liginosulfonic acids (Craig and Logan 1962).

Lignin nitration is used in delignification of hardwoods and grasses in western Europe (Nikitin 1966); nitrolignins are formed. Lignins also react readily with nitrogen dioxide. 3,5-Dinitroguaiacol has been isolated from nitrolignins. Wood lignins can be chlorinated and then dissolved in sodium sulfite or alkali. The chlorination of lignins has a practical application in the delignification of plant material to prepare pulp from wood, straw, grasses, etc., and in bleaching technical-grade pulps. In addition to chlorine bleaching, hypochlorite or hydrogen peroxide bleachings are also used. The reactions between hypochlorite and lignins involve chlorination of the aromatic rings, side-chain decomposition, and cleavage of the lignin molecule. The reactions are a function of the pH. Substitution reactions are slower at high pH and oxidation to quinone structures is faster (Nikitin 1966).

Hydrogenation and hydrogenolysis techniques can be employed to produce phenolic compounds from lignins. By using Raney nickel catalyst in the hydrogenation of maple wood lignin, Brewer et al. (1948) isolated 10%-15% of the lignin present as compounds I, II, and III shown in Fig. 3-3, which have the aromatic nuclei intact. If the hydrogenation is carried out with copper chromite catalysts at high pressure, hydrogenation of the aromatic rings can occur, and propylcyclohexane derivatives can be isolated in high yields (see, for example, Harris et al. 1938). By reduction with sodium in liquid ammonia, Shorygina et al. (1947, 1948, 1949, 1950) isolated 28% of the lignin present as compounds IV and V from spruce cuproxam lignin. The hydrolysis or ethanolysis of lignins also produces phenolic compounds (see Sarkanen 1975). The autoclaving of spent pulping liquors at 300°C in the presence of Na₂S yields 33% of ether-soluble phenols, along with various organic acids, mercaptans, lactones, and sulfides (Enkvist et al. 1962).

Hydrocarbon Research, Inc. (1980) is developing a two-step process to convert kraft lignin to phenol and its derivatives. The technique involves a fluidized-bed hydrocracking with a proprietary catalyst formulation, followed by a thermal (noncatalytic) hydrodealkylation (30% conversion efficiency per path). Yields (by weight) are 20% phenol, 14% benzene, 13% fuel oil, and 29% fuel gas. The presently used catalyst has 56% selectivity for phenol. Increasing catalyst selectivity and hydrodealkylation efficiency, and minimizing repolymerization of the free radicals as well as hydrogenation of the aromatic rings, could increase the phenol yield of the process.



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Figure 3-2. Proposed Structure of Beech Lignin by Nimz (1974)

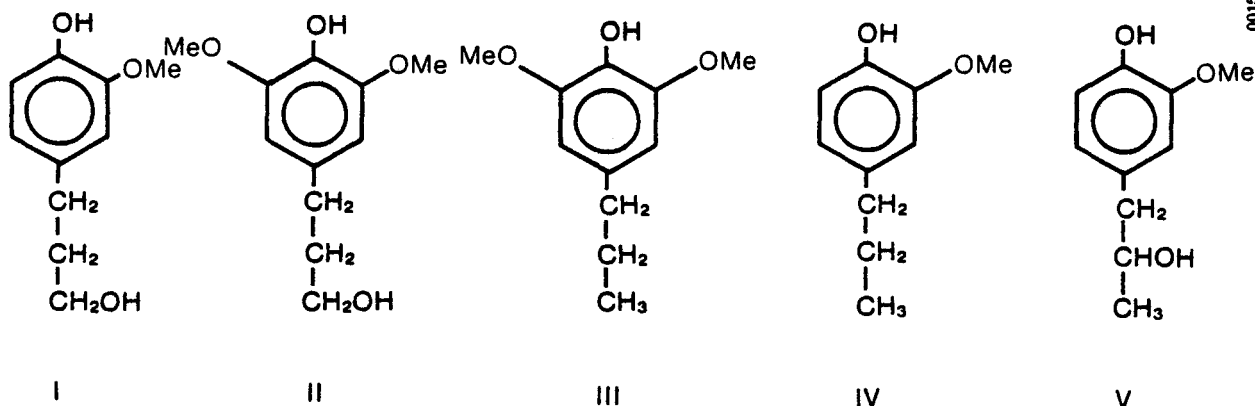


Figure 3-3. Isolated Phenyl Propane Products of Lignin Hydrogenation and Degradation

In this section the electrochemistry applied to lignins of some species is described. Most of the literature on this subject originated in the Soviet Union and was available chiefly as abstracts from Chemical Abstracts or the Institute of Paper Chemistry through the beginning of 1980. Exact information concerning the origin of the lignins, specific reaction products, etc. often was lacking. Most likely, the lignins used in the work described were poorly characterized and the work was of an exploratory nature.

Electrochemical oxidations provide a greater selectivity and means of control of oxidation. Therefore, these studies might give a better understanding of the degradation of lignin polymers and the oxidative dehydrogenation of lignin monomers. Electrochemistry can also play an important role in the study of delignification during oxygen pulping (see Landucci 1978; Landucci 1979; Landucci and Sanyer 1975) and in the assessment of the influence of transition metal ions on these processes.

Pyrolysis chars of lignin have semiconducting properties; they might be used as depolarizers or electrodes. Because of the similarity of these chars with those obtained from coal (coke) or peat, the electrochemistry of the latter is also discussed. Most of the problems in coal or coke use caused by high sulfur and ash contents can be minimized by the use of vegetable charcoals.

3.1 THE ELECTROCHEMICAL OKIDATION OF LIGNINS

3.1.1 Synthesis of Low-Molecular-Weight Carboxyl- and Carbonyl-Containing Compounds and of Electrolytically Modified Lignins with Improved Physicochemical Properties

König (1921) investigated the electrolytic oxidation of lignin. Vanillin was detected among the oxidation products.

Bailey and Brooks (1946) studied the electrolytic oxidation of butanol lignin in NaOH. Lead electrodes were used with a current density of 2 A/cm^2 for 48 hours. The products obtained were methylethylketone (23%), acetone (15%), acetic acid (15%), aromatic acids (24%), oxalic acid (3%), and isobutylmethylketone (~2%).

Kovalenko and coworkers (1973a, 1973b, 1976a, 1977) and Smirnov et al. (1975) have studied the electrochemical oxidation of hydrolysis lignins (see Hoyt and Goheen 1971, p. 858), aiming at the production of low-molecular-weight carbonyl- and carboxyl-containing compounds. They sought also the formation of a modified lignin, containing extensive accumulation of COOH and phenolic OH groups, which would have increased reactivity, for instance, when used as a filler and hardener (see Hoyt and Goheen 1971, p. 854) in epoxy resins (Kovalenko et al. 1976b). The objective of the work was the conversion of hydrolysis industry wastes of lignin (probably from wood saccharification processes) into more suitable products by electrochemical means (Smirnov et al. 1975).

Kovalenko et al. (1973b) described electrochemical oxidation experiments using hardwood hydrolysis lignin in ammonium hydroxide. In this medium nitrogen was introduced as amide groups into the modified lignin. The influences of the anode material (nickel, platinum, ruthenium oxide, or graphite) and of the temperature ($25^\circ\text{--}75^\circ\text{C}$ range) were investigated. Current efficiencies from ~20% (Ni anode) to ~50% (RuO) were reported, and they increased with increased temperature. Graphite and ruthenium oxide yields of oxidation products were higher than those on platinum and nickel. The oxidation products were determined by paper and gas chromatography. The major fractions obtained were (1) aldehydes (2%–5%), including vanillin (or 4-hydroxy-3-methoxybenzaldehyde), isovanillin (or 3-hydroxy-4-methoxybenzaldehyde), trimethoxybenzaldehyde, and veratrylaldehyde (or 3,4-dimethoxybenzaldehyde); and (2) acids (5%–15%), including syringic (or 4-hydroxy-3,5-dimethoxybenzoic), o-hydroxybenzoic, and o-hydroxypropionic acids. In addition, one- to eight-carbon aliphatic acids (~1.5%) were obtained from the oxidation of side chains. The addition of chemical oxidants such as cerium(IV), hypochlorite, and periodate increased the rate of oxidation.

Kovalenko and co-workers (1976a, 1977) continued these studies with the electrochemical oxidation of softwood hydrolysis lignin in sodium hydroxide. The lignin used in the electrochemical experiments was made totally soluble and more reactive by heating in 20% NaOH at 180°C and 10 atm in a pressure reactor for 2.5 hours. The nature of the anode was varied (Pt, Ni, Cu, or graphite). The electrolyses were performed at $\sim 70^\circ\text{C}$, to the extent of 1 Ah/g lignin (current densities of $2\text{--}5 \text{ A/cm}^2$). Table 3-2 compares the yields of

Table 3-2. Yields of Low-Molecular-Weight Degradation Products and Changes of the Functional Composition of Lignin after Electrochemical Oxidation

Anode Material	COOH (meq/g)	OH _{phen} (meq/g)	Vanillin (%)	Vanillic Acid (%)	CO ₂ (%)	Aliphatic Acids (%)
Platinum	3.30	3.48	2.0	1.5	7.6	4-5
Nickel	2.48	3.21	2.2	1.0	6.8	3-4
Graphite	2.03	4.75	0.2	0.1	11.3	5-6
Copper	1.72	5.30	0.2	0.1	12.8	6-8

Source: Kovalenko et al. 1977.

Note: Lignin concentration in anolyte = 50 g/L.

low-molecular-weight degradation products and the changes in COOH and phenolic OH contents of the modified lignin after electrolysis with the various anodes. On Pt and Ni the highest product yields of mild oxidative decomposition (vanillin and vanillic acid) were equivalent to yields of chemical oxidation with nitrobenzene under comparative conditions (Kovalenko et al. 1977). On Cu and graphite, higher yields of fatty acids and CO₂ and lower yields of the aromatic derivatives were observed, suggesting that these electrodes provide more favorable conditions for oxidative degradation. Table 3-2 also shows that the functional composition (COOH, phenolic OH) of the modified lignins depends on the nature of the anode material. The content of OCH₃ groups in the oxidized lignins decreases from 13.5% to 3.5%, suggesting that the electrochemical oxidation is accompanied by demethoxylation. On Pt and Ni the oxidation process might be a two-electron step followed by demethoxylation, yielding quinonoid-type structures. Prolonged electrolysis at Pt or Ni increases the phenolic OH content (Fig. 3-4). On Cu and graphite a yield of phenolic OH groups higher than the content in the starting material was observed. The explanation given for these high phenolic OH contents was the formation of polyhydric phenols. The lignins oxidized at Pt or Ni have higher COOH content than those oxidized on Cu or graphite (Table 3-2). The time of electrolysis significantly affects the yields of low-molecular-weight degradation products (see Fig. 3-5). The yield of vanillin and vanillic acid reaches a maximum at about 1 A h/g lignin and decreases continuously with increased electrolysis time, whereas the yield of CO₂ and of fatty acids increases.

Davydov et al. (1976b) have performed similar constant-current electrolyses experiments with lignosulfonic acids (2%) in 2.5 N NaOH on platinized Pt or bright Pt electrodes. Changes in the oxidized lignin included increased COOH and phenolic OH content, in agreement with the results reported above. Decarboxylation occurred at current densities greater than 32 mA/cm². The properties of the modified lignins permit their use as chelating sorbents (see Hoyt and Goheen 1971, pp. 856-7). In these studies the addition of foreign ions as charge carriers was not beneficial. Increased temperature favored both electrochemical oxidation and degradation.

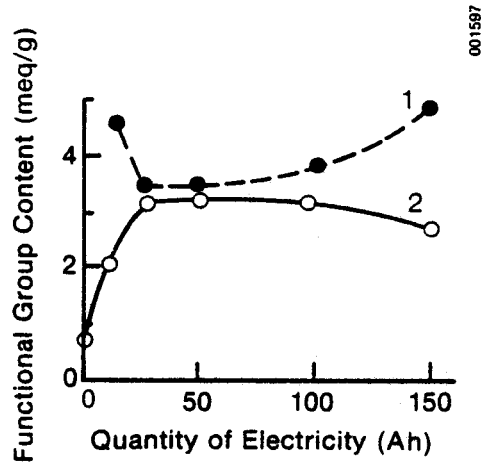


Figure 3-4. Dependence of the Functional Composition of Lignin Oxidized on a Platinum Electrode on the Electrolysis Time. (1) Phenolic OH; (2) COOH. From Kovalenko et al. 1977.

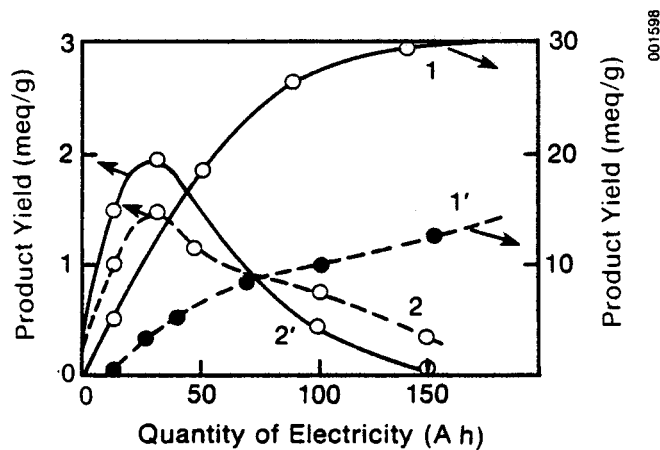


Figure 3-5. Dependence of the Product Yields of the Lignin on a Platinum Anode as a Function of the Electrolysis Time. 1: CO₂; 1': aliphatic acids; 2: vanillic acid; 2': vanillin. From Kovalenko et al. 1977.

Forostyan et al. (1976) have also reported studies of the electrolytic oxidation of softwood hydrolysis lignin, apparently using the same type of lignin employed by Kovalenko et al. (1976a, 1977), but without a previous high-temperature alkaline treatment. The electrolytic suspension of the lignin in 5% KOH was degraded and decarboxylated and formed a water-soluble phase. The same polymer under electrolytic oxidation in 20% H₂SO₄ did not undergo significant changes.

Gorokhov and Krayanskii (1971) have reported studies on the electrochemical oxidation of hydrolysis lignin from cotton hulls. The lignin was washed free of water-soluble acids to give 81.8% lignin and 1.4% ash. The oven-dried lignin was pretreated by heating at 70°C for 1 hour (1 g lignin, 0.3 g NaOH, 0.26 g H₂O), after which reflux with aqueous NaOH for 5 hours rendered two-thirds of the lignin soluble. The filtrate was subjected to electrochemical oxidation at 25°C at a constant current of 2.5 A for 4 hours, during which the voltage increased from 6 to 12 V. The pH of the solution decreased from 13.5 before the electrolysis to 9.1. The number of free reducible groups (COOH) increased. The originally dark brown solution was also partly bleached after oxidation. The analysis of products is not reported in the abstract.

3.1.2 Voltammetric Oxidation of Lignins

Mechanistic studies of the anodic oxidation of sulfate lignin in alkaline medium were performed by Kozhevnikova and Zaitseva (1978) on a rotating platinum disk electrode. The order of the reaction was found to be 0.4 and the voltammograms indicate slow electron-transfer reactions. The electrooxidation current was linearly dependent on concentration in alkaline solutions at potentials of 0.8-1.2 V.

Vodzinskii and co-workers (1974, 1975) and Koryttseva et al. (1978, 1979a, 1979b) have investigated the anodic voltammetry of various lignins--protolignins, spruce dioxane lignin, lignosulfonic acids, lignosulfonates, milled wood lignin, and hydrotropic lignin--on a pyrolytic graphite electrode. These authors have found that the half-wave potential $E_{1/2}$ ranges from 0.23 to 0.33 V (against the normal hydrogen reference electrode). Several preparations of protolignins yielded $E_{1/2}$ of 0.23-0.30 V. For spruce dioxane lignin the $E_{1/2}$ was 0.25 V, whereas all lignosulfonate derivatives gave 0.33 V. Guaiacol (or 2-methoxyphenol) under the same conditions had a $E_{1/2}$ of 0.33 V, whereas phenol, p-cresol, 2,6-dimethoxyphenol, pyrocatechol, vanillin, and tannin gave $E_{1/2}$ 0.2-0.25 V more anodic. The $E_{1/2}$ potentials for these lignins were dependent on pH but essentially independent of concentration or the potential scan rate. The electrochemical behavior of the lignins on the graphite electrodes was found to be adsorption-diffusion controlled. The electrochemical oxidation current varied linearly with the concentration of the lignins or model compounds. Based on the $E_{1/2}$ differences, an analytical method was developed to determine the concentrations of lignins (e.g., lignosulfonic acids and phenol in pulp mill effluents). The voltammetric analysis was found to be more accurate than the colorimetric analysis (Koryttseva et al. 1979b; Vodzinskii et al. 1974, 1975).

3.1.3. Electrochemical Halogenation or Oxidation Related to the Pulp and Paper Industry

Pershina (1968) investigated potential uses of industrial wastes of hydrolysis lignins. She described electrochemical chlorination yielding modified chlorinated lignins utilized for the preparation of Bakelite-type molding powders.

Demin et al. (1979) described electrochemical oxidation experiments with dioxane lignin in NaCl (3%) at constant current ($\sim 12 \text{ mA/cm}^2$). The lignins were extensively degraded and chlorinated. A process for selective electrochemical bromination of lignosulfonic acid and lignin from kraft pulping processes is described in the patent literature by Zeigerson et al. (1974). The electrolyte contained $\sim 14\%$ HBr and $\sim 7\%$ HCl, and the electrochemical halogenation was performed on a Ti anode using an average current of $\sim 50 \text{ mA/cm}^2$.

Several attempts have been made to utilize electrolysis of waste liquors (black, sulfite, etc.) to increase pulping yields. Most of the modified lignins were separated by filtration or flotation, and the pollution was decreased (e.g., Shinn 1945; Santiago 1971; Hara 1971; Ichiki and Ishii 1974; Malkov et al. 1976).

In the wood and wood pulp industry, where chlorination processes play an important role in pulping and bleaching, the halogenation reactions were extensively studied (Dence 1971). To a much lesser extent, electrochemical chlorination has also been studied in connection with bleaching and pulp recovery and waste liquor treatments (examples: Kashihara 1972; Ohta 1974; Vulchev et al. 1974; Buczylo 1975; Selivanov et al. 1976; Davydov et al. 1976a and 1976b; Anisimova and Babkin 1978; Demin 1978; Serdobol'skii et al. 1978). More systematic studies have been performed of the changes in lignins as a function of the electrolyte composition during electrochemical bleaching of pulp (Demin et al. 1976). In addition, Coskuner (1972) studied the resulting chlorinated lignins extracted as a function of electrolysis time.

3.2 THE ELECTROCHEMICAL REDUCTION OF LIGNINS

3.2.1 Reductive Degradation and Polymerization

Itoh et al. (1968) described electrolytic reductions in alkaline (1 N NaOH or LiOH) suspensions of Klason lignin and compared the solubilization of the electrolytic process with that of alkaline hydrolysis only. Lead cathodes and copper anodes were employed, and the current density was 30 mA/cm^2 . The temperature in the cathode compartment containing the lignin suspension was 55°C . After 10 hours of electrolysis 70% of the lignin dissolved, as compared to 60% from the alkaline hydrolysis. Continued electrolysis of isolated fractions increased solubilization.

Chupka et al. (1976) described the electrochemical reduction of dioxane lignin and kraft lignin in NH_3 solutions by ammonium amalgam, which was continuously regenerated electrochemically. During electrolysis substantial degradation took place in addition to reduction. The degree of degradation of these lignins increased linearly with the increase of NH_3 concentration in

solution. The degradation products were low-molecular-weight monomeric and dimeric units, which were very unstable and polymerized in air.

3.2.2 Polarographic Studies of Lignins

The polarographic reduction of protolignin in 0.1 N NaOH at 25°C gave irreversible polarograms which indicated adsorption of the lignin on the mercury electrode (Evstigneev et al. 1978a). Gorbunova and Bogomolov (1973) reported half-wave potentials of -1.0 to -1.35 V for milled wood, dioxane, alkali, and sulfate lignins obtained from treatments at 120° to 180°C (LiOH electrolyte). These values became less cathodic with more vigorous conditions of lignin extraction from the wood, corresponding to an increased formation of easily reducible quinonoid structures.

Koval'skaya et al. (1978) studied lignin-containing fractions obtained after steaming wood chips at 160°-170°C. The ether-soluble fraction consisted of aromatic carboxylic acids, separated from phenols and neutral compounds by extraction with NaHCO₃. The phenols were then separated by extraction with NaOH. Electrochemical reduction of the ether fraction at -1.6 to -1 V produced an increased amount of high-molecular-weight fractions of aromatic acids and phenols. Electrochemical reduction of the acid fraction, neutralized by alkali, at -0.8 to -1.2 V resulted in accumulation of low-molecular-weight components due to degradative reduction. The same treatment of the phenol fraction (phenol; o-, m-, p-cresols; 3,4,5-trimethylphenol; and vanillin) caused crosslinking.

Evstigneev et al. (1978b) studied the polarographic behavior of protolignin in dioxane/H₂O (9:1 ratio) and in dimethylsulfoxide (DMSO). In the mixed solvent and in DMSO the electrochemical reaction on the dropping mercury electrode (DME) is irreversible and the lignin is adsorbed on the electrode. The largest number of reduction waves and elimination of adsorption was reported for DMSO with tetrabutylammonium perchlorate as the supporting electrolyte. Stromskaya and Chupka (1978) reported four reduction waves for dioxane lignin in dimethylformamide with 0.5 M tetraethylammonium bromide as the supporting electrolyte. All waves were totally irreversible. Kraft lignin gave only one irreversible wave under these conditions.

Studies of the polarography of thiolignin and of the effects of cooking products of alkaline treatments were performed by Kanda and Kawakami (1957, 1959) and Terashima et al. (1968). They systematically investigated the influence of cooking on the polarographic catalytic waves in a cobalt(II)/NH₄Cl/NH₃ buffer.

3.3 THE ELECTROCHEMICAL DELIGNIFICATION OF PLANT MATERIALS

Sychev and Petrova (1954) placed plant materials (straw, hulls, etc.) in a cathode cell containing 3% NaCl. The anode compartment also contained 3% NaCl. Electrolysis at ~32°C, in which the Cl₂ gas evolved in the anode was removed, yielded in the cathode compartment a material suitable for animal feeds. A second electrolysis in 0.5% NaCl yielded a bleached and de-ashed product suitable for hydrolysis. Over 40% of the lignin was removed in the

electrolysis. For paper production an additional chemical treatment yielded snow-white pulp. Petrova and Sychev (1955) also studied the morphological and biochemical changes in straw during the electrochemical delignification. This method enabled the production of feed cellulose and a high-quality protein feed. Due to the mild conditions of delignification, the pulp obtained resembles holocellulose and has great mechanical durability.

3.4 THE ELECTROCHEMICAL BEHAVIOR OF PYROLYSIS CHARs OF LIGNINS AND OF ANALOGOUS MATERIALS DERIVED FROM COAL OR PEAT

3.4.1 Chars of Lignins

Steelink and Wilkinson (1975; Wilkinson and Steelink 1975, 1976) have made some preliminary studies of the feasibility of using lignin pyrolyzates as cathodes in primary cells. After the lignins--e.g., kraft and alkali--were pyrolyzed in nitrogen at 600°-1000°C, a material was formed with electrical resistance in the semiconductor range and which was easily machined. The electronic conductivity resulted from structures of the hydroquinone-quinone type present in the pyrolyzates. Similar types of compounds have been used as cathodes in several types of batteries (e.g., Dereska 1976). Wilkinson and Steelink (1975) demonstrated that it is possible to carry out simple chemical modifications of these lignins. Table 3-3 shows the voltage characteristics of some chars of lignin-zinc cells. These electrodes can also be used as anodes if they are electrically charged. Discharge through a 10- Ω load reduced the voltage from 1.28 V to 0.34 V versus Ag/AgCl after 1 hour because of polarization effects. The advantages of these materials are the thermoplasticity and electrical properties after pyrolysis, which produces a cohesive solid; the ability to be chemically modified before pyrolysis or by controlled-potential electrolysis after pyrolysis; and, finally, the abundance and the low cost of these materials.

Table 3-3. Lignin-Zinc Cell Voltages

Lignin Sample ^a	OCV ^b	V _{L,2} ^c	V _{L,12} ^d
Softwood kraft	1.22	1.00, 0.53	0.91, 0.46
Tomlinite	1.24	0.50, 0.17	0.44, 0.10
Nitrated softwood kraft	1.39	1.06, 0.73	1.04, 0.68
Hardwood kraft	1.24	1.04, 0.53	1.06, 0.50

Source: Wilkinson and Steelink 1975.

^aAll samples pyrolyzed under nitrogen for 1 hour at 700°C.

^bOpen-circuit voltage.

^cVoltage measured across 100 Ω resistance. First number is initial voltage; second number is voltage after 2-hour discharge under load.

^dFirst number is initial voltage. Second number is voltage across 100 Ω resistance after a recovery period of 12 hours.

3.4.2 Coke-Type Materials

3.4.2.1 Combined Chemical-Electrochemical Processes in Indirect Fuel Cells

Anbar (1973), Anbar et al. (1975), and McMillen et al. (1977) described a combined chemical and electrochemical process involving a liquid metal anode (e.g., Pb, Sn, or Pb-Sn alloys) and an air cathode with the formation of the metal oxide and production of electricity in the external load. The anode is regenerated by a chemical reaction, and the metal oxide is reduced by carbonaceous fuel (carbothermic reaction). This cycle is carried out in molten carbonate (lithium-sodium-potassium eutectic) in the temperature range of 500°-800°C. Since this molten salt medium effectively scavenges sulfur oxides, atmospheric pollution is inherently minimized. Particulate matter is also prevented from escaping from the molten medium, and the conditions are not favorable to the formation of nitrogen oxides.

The chemical reduction of lead oxide by chars of several origins (petroleum coke, bituminous and lignite chars, graphite, vegetable coconut charcoal) in the molten carbonate ternary eutectic was studied by McMillen et al. (1977). The oxidation is a two-step process involving the rate-controlling reaction of carbon with carbon dioxide to form carbon monoxide, followed by the rapid oxidation of carbon monoxide by lead oxide. The overall rate of carbon oxidation is directly proportional to the accessible carbon area. An activation energy of ~40 kcal/mol was found for all the cokes tested. This energy seems to be associated with the rate-determining carbon monoxide desorption from the carbon surface.

McMillen et al. (1977) tried coupling the electrochemical and the chemical steps in several cell configurations. Materials problems due to the corrosive nature of molten lead and molten carbonates led to cell configurations of the differential-density type: molten lead was at the bottom, and the contact to the molten lead was made from the top through carbon rods, which contacted the molten electrolyte. In these experiments high open-circuit voltages (OCV) were observed (~1 V). In experiments avoiding such contacts, the OCV was ~0.5 V, the calculated thermodynamic potential for the conditions employed (anode sweep gas composition: 67% CO₂, 33% O₂; reference electrode: 14% O₂, 33% CO₂, 53% N₂). These results indicate that the carbon rods were undergoing direct electrochemical oxidation (see Section 3.4.2.2). Figure 3-6 shows the calculated and observed anode voltages as a function of the current density at 800°C; an immobilized electrolyte in an alumina matrix was employed. The difference between carbon contact and no carbon contact is clearly seen in the figure. In the latter case, larger polarization losses were found than in the free electrolyte case. Polarization losses decreased if a layer of free electrolyte was interposed between the matrix and molten lead.

The lead/air cell did not operate satisfactorily as an indirect fuel cell for carbon (or hydrogen or carbon monoxide) (McMillen et al. 1977, p. 38), and current densities of ~20-50 mA/cm² at ~0.3 V were obtained. Tin anodes exhibited a better performance than lead anodes; cell voltages of ~0.7 V at ~100 mA/cm² were obtained at 770°C. The cell potentials were determined by the CO₂ concentration at the anode, which is affected by the composition of the anode purge gas. Practical problems include electrolyte losses and solid carbonaceous fuel cell design.

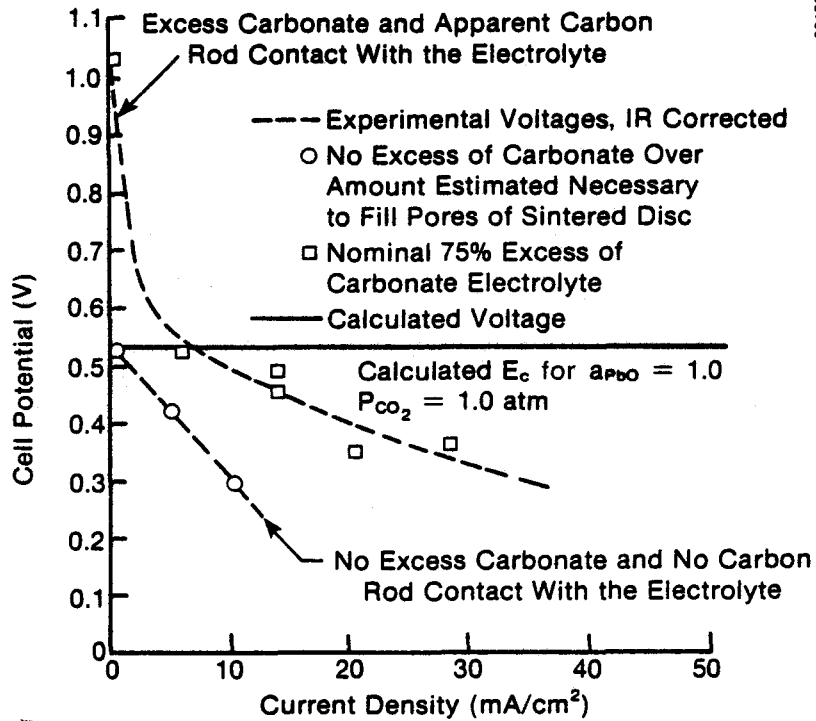
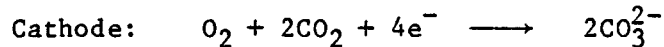


Figure 3-6. Lead Anode Performance with Immobilized Electrolyte. Electrolyte purged with 10% CO₂, 90% CO at 800°C. From McMillen et al. 1977.

3.4.2.2 Direct Fuel Cells with Solid Carbonaceous Fuels and Air

Weaver et al. (1975, 1977, 1979) investigated the direct carbon/air fuel cell in molten carbonate media. The carbon was obtained from coal through a pyrolysis procedure (425°-625°C under pressure) followed by heating at ~1000°C under vacuum. This material is porous and electrically conductive (0.3-0.6 Ω/cm). The overall electrochemical reactions in the cell can be represented as follows:



The coke described above (Stanford Research Institute coal, or SRI coal), spectroscopic carbon, pyrolytic graphite, and a very porous coke-type material prepared from a coal extrusion process at the Jet Propulsion Laboratory (JPL coal) were investigated. Table 3-4 summarizes results supporting the stoichiometry of the net reaction. The last three runs were on pyrolytic graphite

Table 3-4. Summary of n-Run Results^a

Run	% CO ₂	% FRA	% CA	n
I	99.1	100	95	3.8
II	99.7	95	100	4.4
III	99.5	--	100	2.5
IV	100	100	100	2.3
V	99.7	100	95	2.6
VI	99.3	105	95	2.3
VIII	99.6	105	75	4.0
IX	99.6	100	95	3.6
X	99.6	100	95	3.8

Source: Weaver et al. 1977.

^aSee text for explanation of abbreviations.

and the remaining on spectroscopic carbon electrodes. In the table, % CO₂ indicates the ratio of CO₂ content to the CO₂ + CO content in the anodic products, and % FRA represents the flow rate expected from the gas chromatographic analysis of the product formed compared to the ratio of the known carrier gas inlet rate to the observed flow rate (test for leaks). The values for % CA correspond to the equivalent current calculated from the observed flow rate of the carbon oxides with the known current. The final column n presents the faradaic correlation between the total carbon consumed as observed weight loss in electrolysis and the total known charge passed. Nonfaradaic, mechanical losses of the anode were considered responsible for the data with n < 4.

Figure 3-7 presents the OCV of various carbon or graphite electrodes as a function of temperature. Figure 3-8 exemplifies some of the studies of anode polarization and compares potentiodynamic polarization curves for the various types of anodes. The polarization for the carbon anodes decreases from spectroscopic carbon to SRI coal to JPL coal. Cell voltages of 0.75-1 V should be possible at current densities of 100 mA/cm². More extensive studies were carried out including detailed electrode kinetics of pyrolytic graphite anodes. Some investigations of air cathodes were performed. Stainless steel series 300 appeared to perform well (Weaver et al. 1979).

Weaver et al. (1979) also calculated a detailed energy balance for an integrated SRI coal/air fuel cell power plant. Using this energy balance, the predicted voltages of the coal-derived anodes for a current density of 100 mA/cm² are 0.55 to 0.75 V. Whereas laboratory cells consisted of slabs of coal-derived anode moving downwards in the free electrolyte with consumption, other designs were proposed to use a different feed system based on coal-derived anode particles in a basket-type cell. Long-term testing to evaluate the influence of the impurities in the cokes on the fuel cell performance and electrolyte balance and more kinetic studies on the air cathode have not been performed.

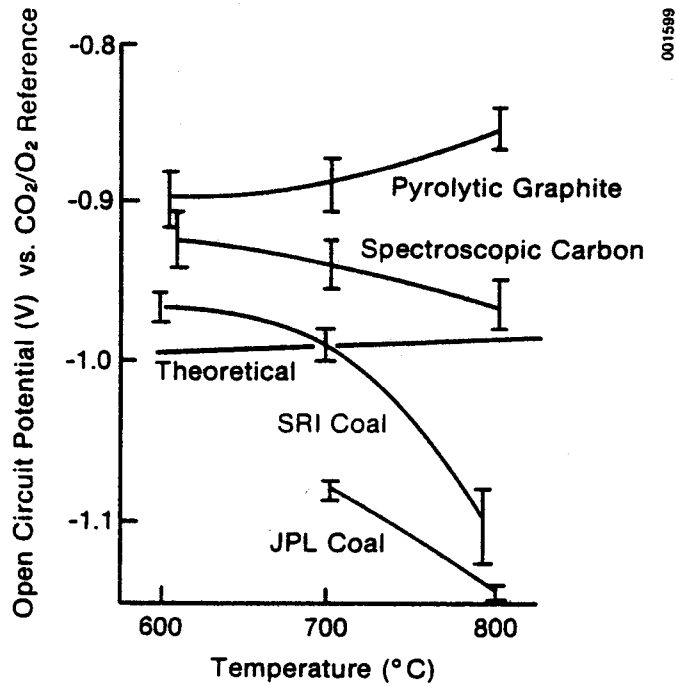


Figure 3-7. Open-Circuit Potential on Various Carbon or Graphite Electrodes. $p\text{CO}_2 = 1 \text{ atm}$. From Weaver et al. 1979.

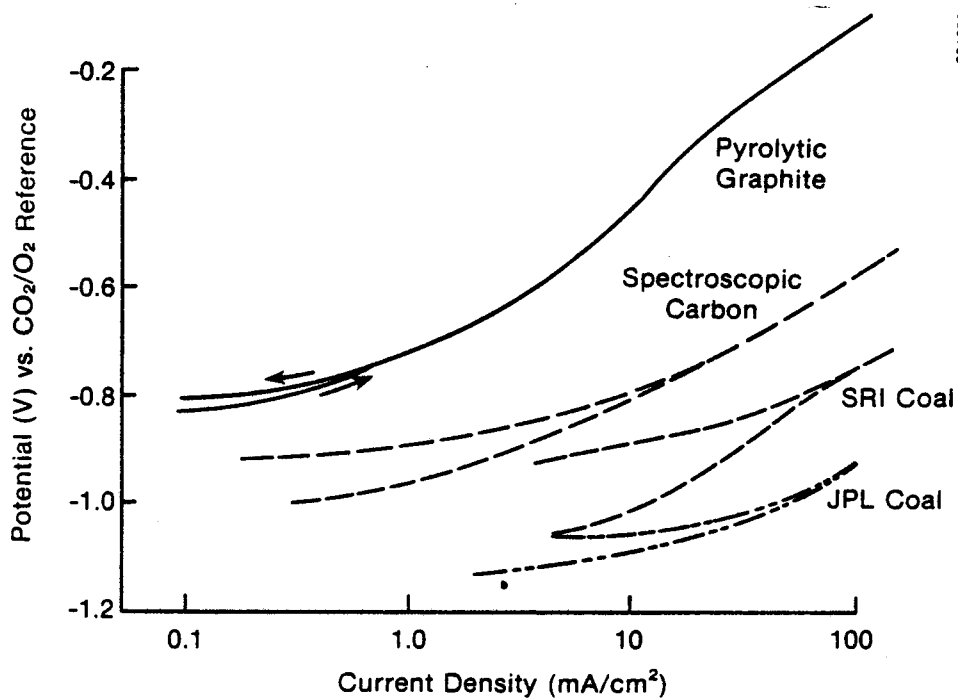


Figure 3-8. Potential Dynamic Polarization Curves at 800°C at a Scan Rate of 1.0 mV/s . $p\text{CO}_2 = 1.0 \text{ atm}$. From Weaver et al. 1979.

3.4.2.3 Depolarizer Behavior: Voltameiotic Processes

Electrochemical processes can be devised to conserve energy, generally by replacing the sacrificial electrochemical reaction with another that operates at a lower voltage. Langer and Sakellaropoulos (1979) have suggested that such processes be called voltameiotic (meiotic is Greek for decreasing); i.e., processes in which the overall electrolytic cell working voltage is reduced by altering the reaction at one electrode. Such processes are not new. The chloralkali industry has utilized air depolarization of cathodes in the sodium chloride electrolysis to reduce the cell initial potential from about 2.15 V to 0.95 V; the cathode reaction is not hydrogen evolution but oxygen reduction to OH^- ions (Kuhn 1971). These processes are also employed in hydrometallurgy. Coal-based electrowinning processes are also known (e.g., Farooque and Coughlin 1979a).

Coughlin and Farooque (1979; Farooque and Coughlin 1979b) have used coal as an anode depolarizer in the cathodic production of hydrogen (water electrolysis) in 4-6 M H_2SO_4 . Figure 3-9(a) shows potential-current density curves as a function of total carbon consumption. The effect of coal concentration on the current density is exemplified in Fig. 3-9(b) at three different temperatures. The coal utilization is not total. The formation of tars in the anodic chambers has been observed. Detailed studies on the effects of coal particle size, concentration, temperature, supporting electrolyte, and coal morphology are given in Farooque and Coughlin 1979b. At the cathode pure H_2 is liberated, whereas at the anode CO_2 and a small percentage of CO are the reaction products.

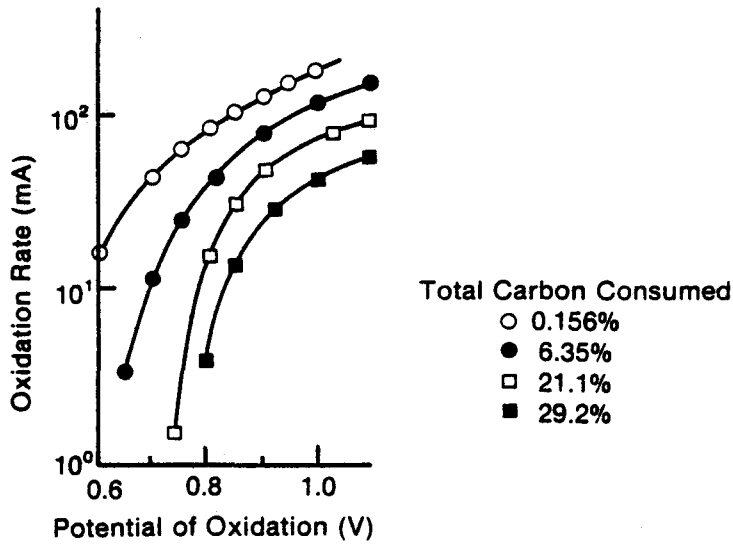
3.4.2.4 Other Systems

Khunkar and Aminul (1972) described the electrolytic oxidation of humic acids from peat. At room temperature with V_2O_5 catalyst, 60% of the peat was converted into oxalic acid and the remaining to CO_2 . The anodes investigated were Cu, Ni, and Pb. Other studies of electrolytic oxidation of coals in alkaline solution (Gaberman and Yushkova 1969; Gaberman et al. 1967) also produced polycarboxylic acids (50%-70% yield), with oxalic acid being the major product.

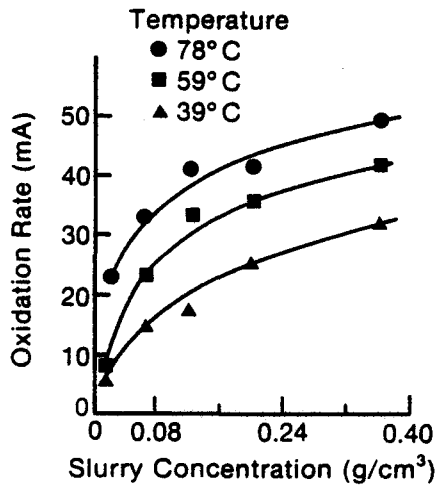
A humic acid (derived from peat) fuel cell has been described by Sakikawa and Nakamura (1965). The positive pole was a porous carbon or a silver-containing porous carbon electrode; the negative pole was Ni, Pd, or Pt. Humic acid was dissolved in 30% KOH. Oxygen gas was passed into the solution from the positive pole. The discharge characteristics of the cells were measured, and OCVs of ~0.5 V were obtained. The silver-containing carbon/Pt combination performed best (0.25 V at 20 mA, 80°C), discharging a constant ~20 mA for 1 hour. The voltage decreased from 0.25 to 0.23 V during that time on an 11- Ω load.

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(a) Effect of Potential on the Oxidation Rate as the Reaction Proceeds. North Dakota lignite; coal slurry conc., 0.069 g/cm³; supporting electrolyte, 5.60 M H₂SO₄; particle size, 125-149 μm; temperature, 114°C; anode area of 96.5 cm².



(b) Effect of Coal Concentration on the Oxidation Rate. North Dakota lignite; particle size, 44 μm and below; supporting electrolyte concentration, 4.13 M H₂SO₄; oxidation potential, 1.00 V; anode area of 6.5 cm².

Figure 3-9. Cathodic Production of Hydrogen in a 4-6 M H₂SO₄ with Coal as an Anode Depolarizer

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SECTION 4.0

CONCLUSIONS AND RECOMMENDATIONS

4.1 SUMMARY

The electrochemical reactions of the main polymeric materials that compose biomass--cellulose, hemicelluloses, lignins, and starch--and of the chief monosaccharides have been reviewed with emphasis on the electrosynthesis of organic compounds and the generation of electricity in fuel cells.

In general, the successful electroorganic syntheses using biomass-derived compounds produced specialty chemicals of low volume, such as dialdehyde starch, calcium gluconate, and sorbitol. Calcium gluconate and sorbitol are presently synthesized by chemical methods: air oxidation and catalytic hydrogenation, respectively. These chemical processes are less energy intensive than the corresponding electroorganic syntheses (see Electrochemical Technology Corp. 1979). If these two electrochemical syntheses were paired, however, the economics might become favorable. The starch derivative synthesis is an example of a very successful electrochemical process. The project was discontinued because of the lack of a market for the dialdehyde compound.

Most of the synthetic work reported here that reached pilot scale or commercialization was performed 30 to 50 years ago. Therefore, it did not enjoy the progress in the science and technology of electroorganic synthesis of recent years. In many cases, the syntheses described were carried out in batch rather than continuous processes due to the lack of proper cells. Electrochemical engineering in recent years has produced a variety of cell configurations--parallel plate, packed bed, fluidized bed, capillary gap, trickle tower, pumped slurry, pump cells, etc.--that can be utilized for practical syntheses (see Krumpelt et al. 1979). Parallel-plate (or filter press) cells are commercially available with a variety of electrodes and separators (Carlsson et al. 1982).

Much basic research needs yet to be done on the application of electrochemical processes to biomass polymeric materials. This research should aim at the production of valuable organic chemicals, petrochemical substitutes, and energy-intensive chemicals such as octane and cetane boosters and fuel extenders. Full advantage should be taken of the current research on the pretreatment of biomass to separate polymeric fractions. Investigations of emerging polymeric materials such as steam-exploded wood components and organosolv wood components promise to be useful, offering the advantages of the lower molecular weight of these polymeric materials and of the characteristics of electroorganic processing.

Most of the research reported here, principally on lignin materials, was carried out on poorly defined materials. Future research should be encouraged to look at newly prepared polymeric fractions that are well characterized, leading to well-characterized products. The semiconductive character of pyrolysis chars of lignins and their thermoplasticity deserve further investigation with emphasis on structural surface determination. Chemical and

electrochemical modifications of these chars may yield suitable electrode materials. Due to the low sulfur and ash content of some of the pyrolysis chars of lignins, their use in molten-carbonate fuel cells probably will be more advantageous than the use of coal. Lignin chars could also be investigated as anode depolarizers; e.g., for hydrogen production by water electrolysis.

This report does not address biomass-derived compounds that are obtained from microbiological, chemical, and thermochemical processing of biomass. This subject will be part of a forthcoming publication (Chum and Baizer). We will briefly address here, however, the general area of fermentation products and electroorganic processing. Most fermentation processes lead to dilute solutions. It is possible, with suitable high-surface-area electrodes, to process dilute solutions. Electroorganic research using fermentation products should be encouraged, aiming at the production of water-insoluble products to allow easier separation of compounds.

Research in electroorganic processing should be encouraged that explores

- selective reactions unique to electroorganic processes which cannot be performed by chemical catalytic processes;
- the possibility of utilizing emulsions in electroorganic processes, which would lead to easier separation of products;
- indirect electrochemical reactions, in which the mediator is regenerated electrochemically;
- pairing of useful oxidation and reduction reactions in matched syntheses;
- interfaces at an early stage with electrochemical engineers to facilitate the choice of the best cell design for a specific process; and
- pollution-free electroorganic processes.

The chemical industry's lack of familiarity with electroorganic processing is a major obstacle to its introduction. Electrical energy costs and reactor system costs are not a major fraction of the overall costs. Typically, electricity costs range from 10% to 12% of the total plant operating costs; this is equivalent, for instance, to the cost of some chemical reactants (Coleman and Taylor 1981). Electroorganic reactor costs are also comparable to the costs of conventional chemical processing (Nanis et al. 1981).

The appropriate electrochemical methodology to convert biomass and derived materials into useful chemicals and energy-intensive compounds should be developed. It is basic, long-range research that has a large potential payoff (see Chum and Baizer 1981). The efforts undertaken thus far should be sustained.

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