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Applications of Organic Electrochemistry in the Preparation of Chemicals and Polymer Intermediates

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ABSTRACT

We have defined electrochemical reactions (oxidation, reduction, coupling, etc.) and processes for potentially obtaining useful fuels, chemicals, and/or polymer intermediates from biomass-derived raw materials. Advantages of electrochemical processing include room temperature reactions, high driving forces, energy efficiency, and operability in relatively dilute solutions. Additional potential advantages are higher yield of desired products, easier separations, higher concentrations of final products (in process solutions), and the ability to "tailor the reaction to produce more of a specific product and/or different products."

INTRODUCTION

Presently, most fuels, chemicals, and polymers are derived from petroleum or natural gas [1]. Before petrochemicals became the raw materials for making chemicals more than 35 years ago, coal was the raw material from which chemicals were made. The renewable agricultural resources and coal are potentially two attractive sources of energy and feedstock for chemicals and polymers. However, biomass may ultimately become a primary source of organic chemicals, plas-

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tics, and petrochemical feedstocks. Thus, biomass may in part produce the energy needs during the next century [2-4].

Chemically, biomass is a cellulosic material composed of 30-40% α-cellulose, 20-40% hemicellulose, and 5-25% lignin. Hemicellulose, a polysaccharide, can be readily hydrolyzed to pentoses (C_5 sugar). α-Cellulose, a linear polymer of glucose, is difficult to hydrolyze to its monomer (glucose) without the formation of degradation products [5, 6]. Resistance to hydrolysis of native cellulose is due to crystalline structure, hydrogen bonding, and close association of microfibril "bundles" of linear cellulose with lignin. Cellulose, therefore, does not hydrolyze easily to glucose because of microfibrils encapsulation by lignin as well as due to its crystalline and hydrogen-bonded structure.

Both α-cellulose and hemicellulose can be converted to sugars by hydrolysis, although the former with difficulty. On the contrary, the lignin in biomass is a polyhydric polymer containing condensed phenolic, open phenolic, condensed ether, open ether, and alcoholic groups. Lignin has a high energy value and can be burned.

This paper defines electrochemical reactions and processes with the potential of obtaining polymer intermediates, chemicals, and fuels from biomass-derived raw materials. Recent developments in cellulose conversion technology are also described.

HYDROLYSIS OF CELLULOSIC MATERIALS

The concept of hydrolyzing cellulose to glucose is more than 100 years old. Hydrolysis can be done either by acid or by enzyme. Major shortcomings of acid hydrolysis are acid recovery when concentrated acids are used and the formations of dehydration products that limit sugar yield to 50% when dilute acids are used. Recently, a twin-screw extruder device has been used in a high temperature (450°F) acid hydrolysis (sulfuric acid) process for conversion of wood pulp to glucose [7]. The combination of high temperature and 20 s hydrolysis time resulted in 60% yield of glucose while avoiding acid-catalyzed degradation.

In enzyme hydrolysis, side products are not formed and the enzyme-catalyzed reactions can be conducted at nearly ambient conditions. The enzymes that promote saccharification of cellulose are β-(1→4)-glucan-glucanohydrolases (EC 3.2.1.4) and β-glucosidases (EC 3.2.1.21). By acting together these enzymes degrade cellulose to cellodextrins, which are water-soluble glucose polymers of about six repeating units, and glucose [8, 9]. Of the many microorganisms examined, the best appears to be Trichoderma reesei mutant, a mold found in soil [10, 11].

Enzyme-catalyzed saccharification of cellulose may be economically viable on a large scale, but certain problems, such as the inability of cellases to hydrolyze native cellulose rapidly and totally

[12] and the inhibition effects that glucose and cellobiose (dimer) have on enzyme action, create difficult areas [13].

RECENT DEVELOPMENTS IN CELLULOSE CONVERSION TECHNOLOGY

Purdue researchers [14] have recently advanced cellulose conversion technology. Their work is based on conversion of the hemicellulose and α-cellulose fractions of native cellulose to pentose (C_5) and hexose (C_6) sugars, fermentation of C_5 and C_6 sugars to fuel ethanol and some limited chemical intermediates, use of lignin fraction to power the ethanol concentration process, and utilization of biomass materials, e.g., agricultural residues and municipal wastes, as raw materials for the process. We shall now briefly describe the Purdue process.

Hemicellulose Extraction

This step is straightforward and involves extraction of native cellulose with dilute acid. Pentose is quantitatively extracted and can be fermented to ethanol or butanediol. The extracted residue consists mostly of lignin and α-cellulose.

Cellulose Pretreatment and Recovery

Lignin seals the microfibrils of highly crystalline linear cellulose. This situation can be reversed by using small amounts of a solvent that swells, disrupts, and ruptures the lignin seals to make the cellulose more accessible to hydrolysis. Cellulose pretreatment solvents that have been used are Cadoxen [15] (4-5% CdO in solution with 25-30% ethylene diamine), chelating metal cellulose swelling agent [16] (aqueous solution of 17% sodium tartrate, 6.6% ferric chloride, 7.8% sodium hydroxide, and 6.2% sodium sulfite), and concentrated sulfuric acid [17]. After pretreatment, a nonsolvent, e.g., methanol and/or water, is added. α-Cellulose is precipitated and the washing can be concentrated to recover the pretreating solvent.

Cellulose Hydrolysis

The pretreated residue can be hydrolyzed by Trichoderma reesei or by acid. The in-situ precipitated α-cellulose has a large surface area which allows the Trichoderma reesei access to the cellulose. The in-situ precipitated α-cellulose is sterilized and fed into an enzyme flask where it is mixed with nutrients and air and innoculated with the fungus. High yields of sugar were obtained with pure microcrystalline cellulose, cornstalks, and bagasse stocks. Following hydrolysis, the lignin fraction can be separated by filtration. Part of the enzyme can be recovered by ultracentrifugation and recycled.

Sugar Fermentation

The C_5 sugar [18] obtained from the hemicellulose can be fermented to 2,3-butanediol by mutant strains of Klebseilla [19] and Aeromonas genera [20]. The C_6 sugar can be mixed with yeast in a controlled environment and fermented to ethanol.

FUNDAMENTALS OF ELECTROCHEMICAL REACTIONS

Table 1 shows the reactions that can be carried out electrochemically. The important electrochemical and chemical parameters by which the reactions can be controlled are indicated in Table 2.

Electrochemistry can introduce up to 3.5 eV to organic compounds (for comparison, photochemistry = 0.8-8.0 eV and radiation chemistry ≈ 80 eV), which means that almost any reaction can be electrochemically carried out. But from a practical viewpoint, we must consider the variables shown in Table 2.

TABLE 1. Electrosynthesis of Organic Compounds

a. Direct electron transfer to generate:

At Anode	At Cathode
Cation radicals	Anion radicals
Dications	Dianions
Carbonium ions	Carbanions
Free radicals	Free radicals

b. Indirect electrolysis:

To generate redox couples
To generate reactive inorganic species, e.g., OH

c. Generation of acid (at anode) or base (at cathode)

TABLE 2. Electrochemical Reactions: Electrochemical and Chemical Parameters

Electrochemical parameters	Chemical parameters
Electrode potential	Solvent/supporting electrolyte concentration
Electrode material	Concentration of starting materials
Current density	Concentration of other components of bath
Electric field	Temperature of bath
Adsorption	pH
Type cell and design:	
Compartmentalized	
Membrane or porous separated	
Static or flow cell	
Solution conductivity	

Let us take a closer look at the factors governing electrode reactions to understand electroorganic synthesis. Figure 1 shows the potential distribution in an operating electrolytic cell [21]. The key factor in determining the selectivity and rate is the electrode potential of both the anode and the cathode. Electrode potential is the difference in voltage between the solid electrode and the adjacent solution. Figure 2 shows that a very large electric field exists ($\sim 10^7$ V/cm) [21]. Because of this, chemical bonds can be introduced into the molecules at low temperatures [22]. Energy levels as a function of applied electrode potential and the intermediates formed are shown in Fig. 2 [22].

Electrosynthesis can be done at constant current (i) or constant voltage (E) as shown in Fig. 3. Since water electrolysis can yield hydrogen (or oxygen), it is important to use a high hydrogen (or oxygen) overpotential cathode (or anode) at which the hydrogen (or oxygen) evolution reaction is very slow. A typical laboratory-scale electrolytic cell for reduction is shown in Fig. 4.

In Table 3 we present some typical electrochemical preparations that can be potentially realized.

Electrolysis of Glucose

Electrolysis of glucose (oxidation, reduction) and biomass-derived C_5 and C_6 sugars can yield important products (Table 4). Electrolytically glucose can be oxidized to useful compounds e.g., saccharic

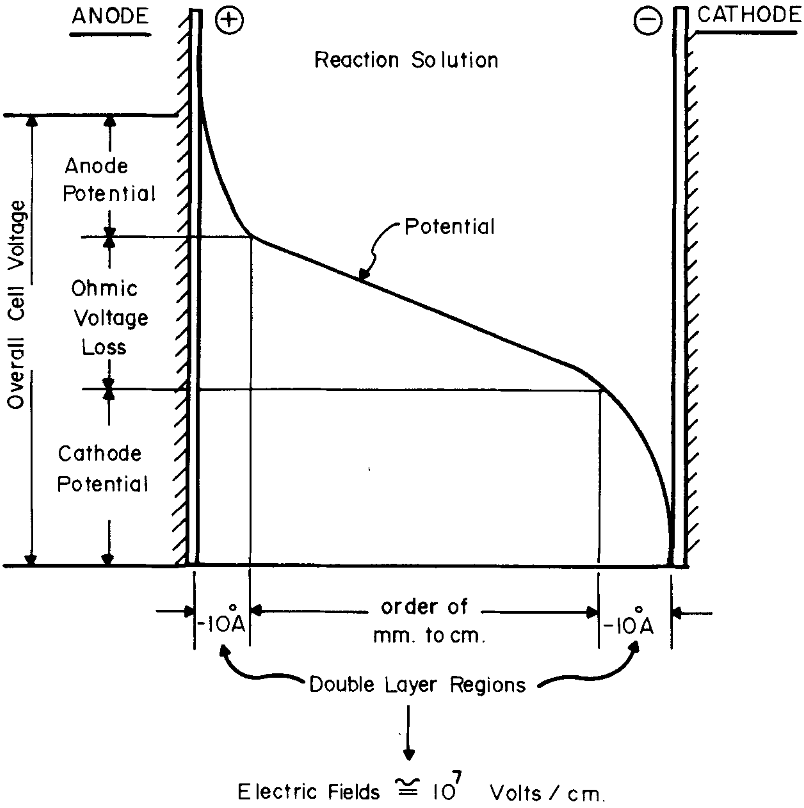
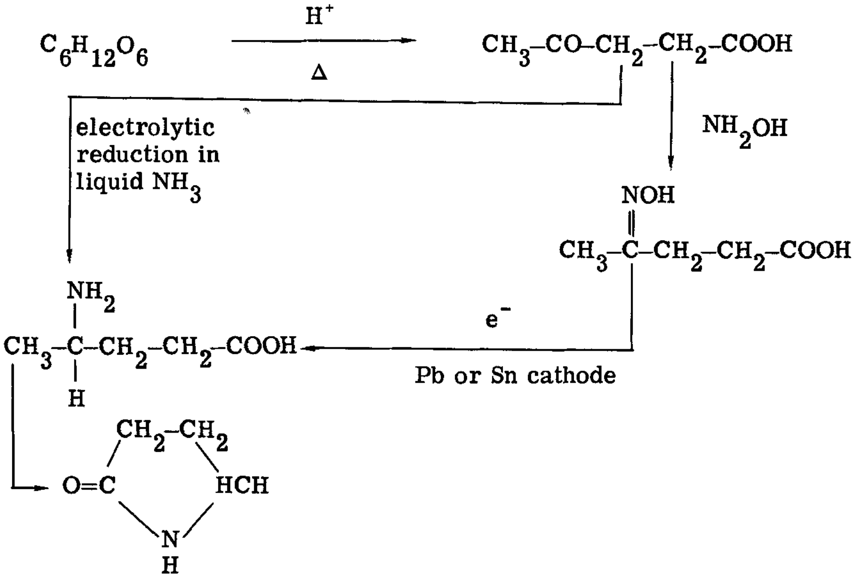


FIG. 1. Cell potential distribution.

acid and tartaric acid. Reduction of glucose produces sorbitol and mannitol. These polyols are useful in the polymer industry to produce polyesters.

We believe some chemicals, e.g., acetic acid, butanediol. acetone, fumaric acid, maleic acid, malic acid, citric acid, and lactic acid, can be more efficiently produced by oxidation or reduction than by fermentation. Additionally, there are some hydrolysis or fermentation products that can be produced efficiently but for which there is no significant market. For example, levulinic acid can be converted in 70% yield from an acidified 3% sucrose solution. We also expect to obtain levulinic acid from the hydrolysis of glucose in similar yield.

Methods to produce polymer intermediates are schematically shown below:



Solvent and/or polymer intermediate

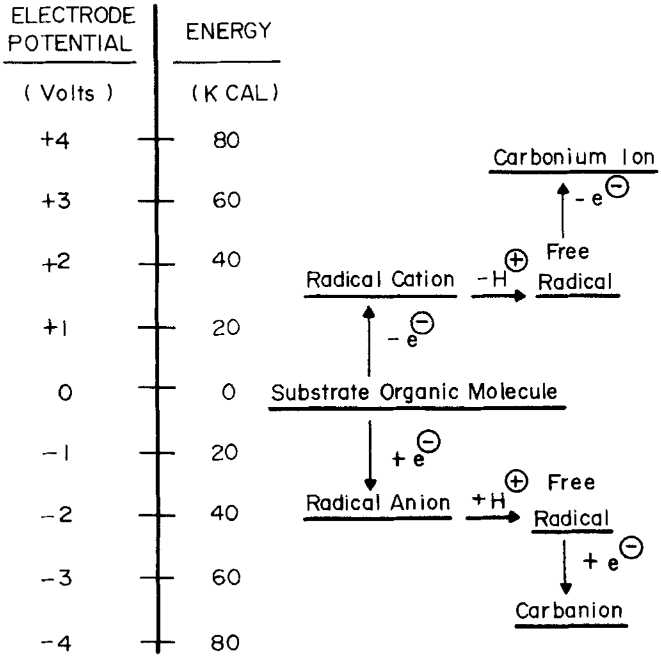
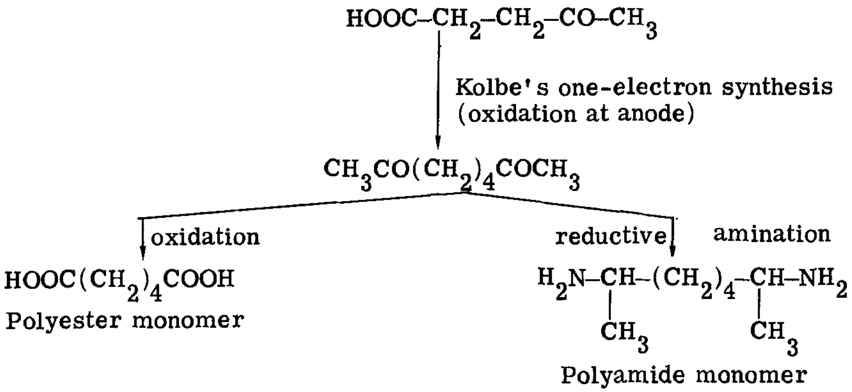


FIG. 2. Energy versus electrode potential. Positive are anode processes, negative are cathodic processes.



$HOOC{-}CH_2{-}CH_2{-}CO{-}CH_3 \rightarrow CH_3CO(CH_2)_4COCH_3$

$CH_3CO(CH_2)_4COCH_3 \rightarrow HOOC(CH_2)_4COOH$

$CH_3CO(CH_2)_4COCH_3 \rightarrow H_2N{-}CH(CH_3){-}(CH_2)_4{-}CH(CH_3){-}NH_2$

Levulinic acid (derived from sugar) and acetaldehyde can be coelectrolyzed by Kolbe's one-electron synthesis to produce methyl propyl ketone (an example of cross-coupling alkonoates). The key requirements for efficient Kolbe coupling in aqueous solution are a Pt anode and high current densities (4 A/cm^2). Another characteristic feature of the reaction is the high anode potential required, usually in the region of +2.2 V (vs SCE). Oxygen evolution, which in aqueous solution begins at about +1.5 V (vs SCE), is more or less completely suppressed by the Kolbe reaction.

Platinized Pt encourages two-electron oxidation. Two-electron oxidation of alkanoates is the favored route if a graphite anode is used. By disproportionation we will be able to produce vinylic compounds which are useful in making polymers.

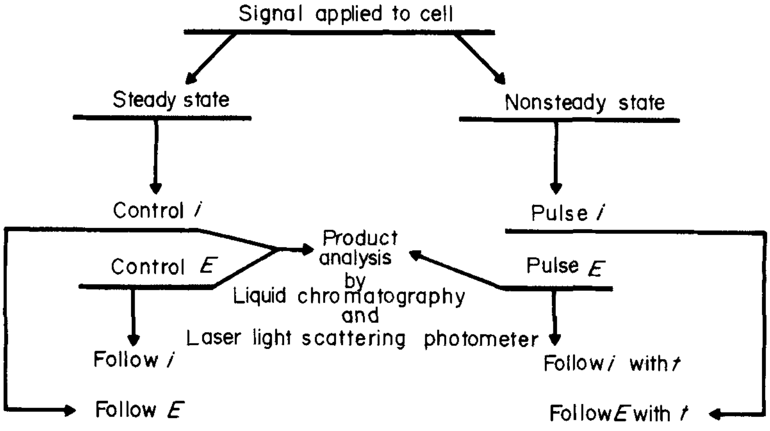


FIG. 3. Methods of conducting electrosynthesis; i is current, E is voltage, and t is time.

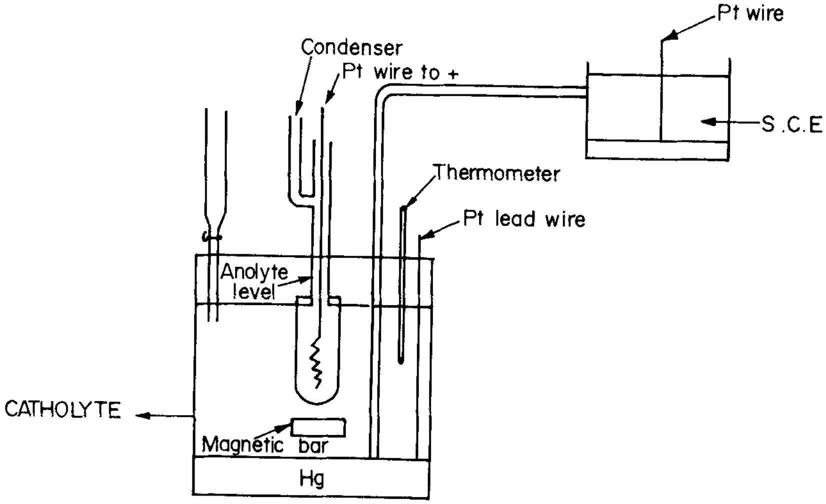


FIG. 4. A typical electrolytical cell for doing reduction; S.C.E. is standard calomel electrode.

Electrolysis of Ethanol and Butanediol

The product of anodic oxidation of ethanol on Pt in aqueous alkaline solution is acetate if the potential is sufficient for oxygen evolution. Oxidation of ethanol to acetaldehyde takes place in aqueous solutions of anode potentials not exceeding +0.8 V versus the hydrogen electrode. It can be achieved at very low current densities, and the final product is acetaldehyde. Other oxidation products from ethanol are shown in Table 5. We wish to point out, however, that ethanol is a useful product by itself, and electrosynthesis will be neither cost effective or potentially useful based on energy considerations.

Butanediol can be successfully oxidized in stages at a Raney nickel anode in basic solution to the corresponding dicarboxylic acid.

CONCLUSIONS

We have defined electrochemical reactions that could be utilized to produce polymer intermediates, chemicals, and fuels from biomass-derived raw materials. Electrochemists and electroengineers are encouraged to advance the concepts described because they could lead to commercialization of some of the processes.

TABLE 3. Proposed Electrochemical Preparations

Substrate, experimental conditions	Anode	Probable products
Ethanol (H_2O, H_2SO_4)	Pt, PbO_2	Acetaldehyde, HOAc, ethylsulfonic acid, ethyl acetate, CO_2
(H_2O, NaOH), cd 5 A/cm^2	C, Pt	CH_3CHO, aldol, CH_4, CO_2
(KOAc)	Pt	Potassium monoethyl carbonate
($NaOC_2H_5$)	Pt	Sodium monomethyl carbonate
($NaOC_2H_5$)	Mg	Magnesium ethoxide, magnesium diethyl carbonate
[$(NH_4)_2CO_3$]	Pt	Acetamidine nitrate
[P, HCl(gas)]	C	Triethyl phosphate
Glucose (H_2O, NaBr, $CaCO_3$)	Fe, Ni, C, Cu, Pb	Calcium gluconate (85-100), calcium 5-ketogluconate (10)
(H_2O, H_2SO_4)	PbO_2	Gluconic acid, arabinic acid, arabonic acid, trihydroxyglutaric acid, saccharic acid, HCHO, HCO_2H, CO_2

	(CH_3OH, $NaOCH_3$)	Graphite	D-Arabinose, D-erythrose, glyceraldehyde
Lignin	(H_2O, NaOH) cd 2 A/cm^2	Pb	$CH_3COCH_2CH_3$ (23.3), CH_3COCH_3 (15.2), HOAc (15.1), β-resorcyclic acid (7.8), 3,4-dihydroxybenzoic acid (7.6), p-hydroxybenzoic acid (4.2), m-toluic acid (3.9), oxalic acid (3.1), isobutyl methyl ketone (1.4)
		Cathode	
Glucose		Hg, Pb	Sorbitol, mannitol
		Pb, Hg, Ni-Al	Formaldehyde
		Pb-Hg, Zn-Hg	Pentose, mannitol, sorbitol, polyhydric alcohols

TABLE 4. Products Obtained from Electrolysis of Glucose

Substrate, experimental conditions	Anode	Probable products
Glucose (H_2O, NaBr, $CaCO_3$)	Fe, Ni, C, Cu, Pb	Calcium gluconate (85-100), calcium 5-ketogluconate (10)
(H_2O, H_2SO_4)	PbO_2	Gluconic acid, arabinic acid, arabonic acid, trihydroxyglutaric acid, saccharic acid, HCHO, HCO_2H
(CH_3OH, $NaOCH_3$)	Graphite	D-Arabinose, D-erythrose, glyceraldehyde
Saccharic acid (H_2O, H_2SO_4)	Pt	Tartaric acid dialdehyde, tartaric acid
Ca gluconate (H_2O, HOAc, $CaBr_2$, CrO_3)	C	Ca-ketoglyconate
Gluconic acid (H_2O)	Pt	Arabinose
Ca 2-keto-D-gluconate	Pt	Calcium D-arabonate
	Cathode	
Glucose	Hg, Pb	Sorbitol, mannitol
	Ni-Al	Formaldehyde
	Pb-Hg, Zn-Hg	Pentose, mannitol sorbitol Polyhydric alcohols

TABLE 5. Electrolysis of Ethanol: Potential Products

Experimental conditions	Anode	Probable products
(H_2O, H_2SO_4)	Pt, PbO_2	Acetaldehyde, HOAc, ethylsulfonic acid, ethyl acetate
(H_2O, NaOH) cd 5 A/cm^2	C, Pt	CH_3CHO, aldol, CH_4
(KOAc)	Pt	Potassium monoethyl carbonate
($NaOC_2H_5$)	Pt	Sodium monomethyl carbonate
[$(NH_4)_2CO_3$]	Pt	Acetamidine nitrate
[P, HCl(gas)]	C	Triethyl phosphate
($NaOC_2H_5$)	Mg	Magnesium ethoxide, magnesium diethyl carbonate

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