Final Undergraduate Research Report  
Anthony Dulaney

The Role of Phenolics in Anode Fouling During Electrolysis of Aqueous Alkali Byproduct Streams from Food and Agricultural Processing
Part 1:
  **Introductory**
  Background Information
  Initial Findings
Part 2:
  Wheat Straw Alkali Extract
  Gas Produced
  Electrode Fouling
Part 3:
  Measuring Phenolics
  Removing Phenolics
Conceptual Biorefinery

Different varieties → Wheat straw → Alkali pretreatment → Liquid (hemicelluloses, lignin & other) → Caustic recovery → Solid (lignin) → Chemical/Physical Modification → Low/high molecular weight products

Cellulose products

Solids (cellulose & other) → Enzyme saccharification → Glucose → S.C. → Ethanol

Lipid → S.C. → Xylose → X.I. → Xylulose

Liquid (hemicelluloses & other) → Enzyme saccharification → Xylose liquor → Polymer products → H₂/hydrogenation → Xylitol

H₂ (gas)

S.C. = *Saccharomyces cerevisiae*, O.Y. = Olegenous yeast, X.I. = Xylose isomerase
In the context of the Penner lab’s biorefinery-oriented research, the primary goal of ongoing electrochemical studies is to generate knowledge pertaining to the chemistry of anode fouling during electrolysis of lignocellulose-derived caustic liquors and, thus, to contribute to implementation of membrane-assisted-electrolysis for alkali recycling during biomaterial processing.
Relatively Long-Term Research Goals

1. Fabricate laboratory-scale continuous flow membrane-assisted electrolysis (MAE) apparatuses for electrochemical studies

2. Generate fundamental knowledge of electrochemical processes dictating the efficiency of MAE applications with lignocellulose-derived caustic liquors
Relatively Short-Term Research Objectives

1. To understand, at a rudimentary level, the basics of simple electrolytic systems

2. To characterize the extent of anode fouling during electrolysis of wheat straw alkali extracts

3. Lay groundwork for future research in alkali recovery
**Electrolysis:** Splitting water with electricity to produce hydrogen and oxygen:

![Electrolysis Diagram](Image from New Mexico Solar Energy Association)
Schematic diagram of two-compartment electrochemical cell for membrane-assisted electrolysis (adapted from Hobbs et al, 1999)

Reactions:

Anode:

$$4OH^- \rightarrow O_2(g) + 2H_2O + 4e^-$$

Cathode:

$$2OH^- + 2e^- \rightarrow H_2(g) + 2H_2O$$
Fouling is the degradation in efficiency of an electrode. Generally through deposition of material on electrode.
How do we approach a research problem?

1. Identify end goals
2. Engineer a path from what we want to know to what we currently know with special consideration of where our competencies lie
3. Gradually increase the difficulty of the experiments
   a. “Science Fair Experiment”
   b. Intermediate Step-Alkali electrolysis
   c. Meeting goals-MAE
Special Considerations for “Science Fair Experiment”

- Understanding why certain reactions are taking place at the electrodes (competing reactions)
- How to use gas capture as an analytical tool (hydrogen and oxygen production and efficiency)
- Basic electrical theories (efficiency)
Special Considerations for WSAE Electrolysis

- WSAE is a complex system (competing anodic reactions)
- Alkali lignin adsorption (anode fouling)
- Amount of hydrogen produced (hydrogen production and efficiency)
- Studies say very little oxygen is produced in Weak Black Liquor which is very similar to our WSAE (oxygen production and efficiency)
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Electrical Terms

- Charge = 1 coulomb = equivalent to the charge of $6.241 \times 10^{18}$ electrons
- Current = 1 amp = $1 \frac{\text{coulomb}}{\text{second}}$
- Work/unit of time = 1 watt = $1 \frac{\text{Joule}}{\text{second}}$
- Work/unit charge = Voltage =
  - $1 \frac{\text{Joule}}{\text{coulomb}}$
  - $\frac{\text{kg} \cdot \text{m}^2}{\text{amps} \cdot \text{s}^3}$
  - $\text{amps} \cdot \text{ohms}$
Understanding Reduction Potential

- Represented as a reduction half-reaction followed by an E/V value
  - \( M^+ + e^- \rightarrow M^0 \) (example half-reaction)

- E/V Value is the ease of a half-reaction to take place measured in volts (CRC)
  - Cathode is a reduction site thus the highest reduction potential happens first
  - Anode is actually an oxidation site so the lowest reduction potential happens first (highest oxidation potential)
Cathodic Reactions in Water

\[ 2H^+ + 2e^- \rightarrow H_2 \quad \text{E/V} = 0.000 \]

\[ 2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad \text{E/V} = -0.8277 \]

Reactions are based on two things:

1. \( E/V \)
2. Concentration
Anodic Reactions in Water

Anode reaction is actually an oxidation

4OH⁻ → O₂ + 2H₂O + 4e⁻ \hspace{1cm} \text{E/V} = -0.401
2H₂O → O₂ + 4H⁺ + 4e⁻ \hspace{1cm} \text{E/V} = -1.229

Anodic reactions represented as:

O₂ + 2H₂O + 4e⁻ → 4OH⁻ \hspace{1cm} \text{E/V} = 0.401
O₂ + 4H⁺ + 4e⁻ → 2H₂O \hspace{1cm} \text{E/V} = 1.229

Reactions are based on two things:

1. E/V
2. Concentration
Autoionization of Water

- $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$
- $[H^+] = 1.0 \times 10^{-7}$
- $[OH^-] = 1.0 \times 10^{-7}$

- Very low concentration of ions

- Ions are crucial for an aqueous electrolysis system
Electrolysis of H$_2$O

- The water ions (H$^+$, OH$^-$) react readily with the electrodes
  - Very low concentrations ($10^{-7}$M)

- The water molecules (H$_2$O) react more slowly with the electrodes
  - Very high concentrations (55M)

- When H$_2$O reacts with electrodes, it leaves ions around the electrodes.
  - Anions around cathodes, cations around anodes
  - Becomes more and more energetically unfavorable to continue moving electrons to a charged area
Electrolytes are attracted to the electrodes causing a much higher concentration than throughout the water:
- Cations move toward the cathode
- Anions move toward the anode

Image from British Broadcasting Corporation
Image adapted from Chang (2009)
Electrolytes “buffer the charge” to reduce the back potential

- Reduce the required voltage
- Some electrolytes react with electrodes
  - E/V
  - Concentration

Image adapted from National Supercomputing Center for Energy and the Environment
Agenda

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  **Initial Findings**

Part 2:
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  Gas Produced
  Electrode Fouling

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Learning the Fundamentals

- **Ideation:**
  - Electrolysis of Water Experiment (Education.com)
  - Hoffaman Apparatus
  - Brownlee Apparatus

- **Execution:**
  - Power Supply
  - Electrodes
  - Inverted graduated cylinders
  - Solution reservoir
Ideal and Assumptions?

Ideal

- All electrons are going into hydrogen production

Assumptions

- All cathodic reactions are producing $\text{H}_2$
- Cathodic reactions are operating at 100% efficiency
- $\text{H}_2$:$\text{O}_2$ ratio $\sim$2
Initial Findings

Gas Produced as Compared to Ideal

<table>
<thead>
<tr>
<th>Gas Produced (cL)</th>
<th>Anode Gas Produced</th>
<th>Cathode Gas Produced</th>
<th>Ratio (Cathode/Anode)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal</td>
<td>2</td>
<td>4</td>
<td>.1M Sodium Citrate</td>
</tr>
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  **Wheat Straw Alkali Extract**
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  Removing Phenolics
What is Wheat Straw Alkali Extract?

-- Alkali processing of plant cell wall materials --

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Using a Hoffaman Apparatus

- Ideation:
  - Building on initial experiment
    - More precise
  - Hoffaman Apparatus

- Execution:
  - Power Supply
  - Electrodes
  - Hoffaman Apparatus
  - Voltmeter
Comparision of Cathodic Gas Produced

- Sodium Citrate
- 5% Sulfuric Acid
- 1% Sulfuric Acid
- 5% NaOH
- 1% NaOH
- WSAE
- Ideal
Comparision of Cathodic Gas Produced

- Sodium Citrate
- 5% Sulfuric Acid
- 1% Sulfuric Acid
- 5% NaOH
- 1% NaOH
- WSAE
- Ideal
Comparision of Cathodic Gas Produced and Anodic Gas Produced

- Sodium Citrate
- 5% Sulfuric Acid
- 1% Sulfuric Acid
- 5% NaOH
- 1% NaOH
- WSAE
- Ideal
Behavior of WSAE Electrolysis on Gas Production

Gas Produced (mL)

- Anode Gas Produced
- Cathode Gas Produced
- Ratio (Cathode/Anode)

- Fresh WSAE, Clean Electrodes
- Old WSAE, Dirty Electrodes
- Fresh WSAE, Dirty Electrodes
Conclusions from Gas Production Experiments

- WSAE had significant non-O2 producing reactions occurring at the anode

- Are the non-O2 producing reactions at the anode correlated with anodic fouling?
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Aqueous Electrolysis of Various Solutions

- 5% Sulfuric Acid
- Sodium Citrate
- 1% Sulfuric Acid
- 5% NaOH
- 1% NaOH
- WSAE
Behavior of Fouling in WSAE Electrolysis

- Fresh WSAE, Clean Electrodes
- Old WSAE, Dirty Electrodes
- Fresh WSAE, Dirty Electrodes
Behavior of Fouling in WSAE Electrolysis

- Fresh WSAE, Clean Electrodes
- Old WSAE, Dirty Electrodes
- Fresh WSAE, Dirty Electrodes
Behavior of Fouling in WSAE Electrolysis

- Fresh WSAE, Clean Electrodes
- Old WSAE, Dirty Electrodes
- Fresh WSAE, Dirty Electrodes

![Graph showing behavior of fouling in WSAE electrolysis](image)
Conclusions from Fouling Experiments

- WSAE showed signs of fouling in two phases
  - First phase takes place in the first 3 minutes with a dramatic jump in voltage
  - Second phase shows a slow fouling over time

- What components of WSAE are responsible for electrode fouling?
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The Role of Phenolics in Foods

- Natural antioxidant
  - Primary antioxidant found in foods

- Mouthfeel and texture
  - In wines, phenolics influence the intensity and type of astringency

- Flavor
  - Raspberry Ketone is responsible for raspberry flavor

- Alkali lignin is a component of WSAE composed of a range of phenolic compounds
  - E/V~0.015-0.60 (Steenken and others, 1982)
Use Folin-Ciocalteu Reagent to assess the phenolic content
  - Commonly accepted measurement of total phenolics

Use gallic acid equivalent (mg GAE/L)
  - Relatively easy to solublize
  - Medium absorptivity (Singleton, 1999)
  - Common measurement of phenolics
Gallic Acid Calibration Curve (Linear Range)

\[ y = 0.0022x - 0.0234 \]

\[ R^2 = 0.9993 \]
Phenolic Content of Common Foods

- Red Wine ~2000 mg/L (Caccetta and others, 2000)
- White Wine ~400 mg/L (Sato and others, 1996)
- Blueberries ~4,100 mg/g (Zheng and others, 2003)
- Cranberries ~3,100 mg/g (Zheng and others, 2003)

- WSAE ~850 mg/L
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PVPP is a common fining agent in wines

Why PVPP?
- Relatively cheap
- Does not affect pH
- Insoluble
PVPP appears to form strong non-covalent associations with selected polyphenolics. The structure depicted above is the hypothetical association between PVPP and the flavonoid catechin.

Level of Treatment versus Phenolics Removed From 25 mL of WSAE

Control
2.132g PVPP
66%
4.264g PVPP
67%
PVPP Treatments at Different pHs

- No PVPP Treatment at pH 13.94
- PVPP Treatment at pH 13.94
- PVPP Treatment at pH 11.86
- PVPP Treatment at pH 10.03
- PVPP Treatment at pH 7.96
- PVPP Treatment at pH 5.86
- PVPP Treatment at pH 3.8*
The Effect of Different Treatments on Phenolic Content

Concentration (GAE mg/L)

- No treatment: 78%
- PVPP, no pH treatment: 76%
- pH treatment: 35%
Conclusions from Phenolic Stripping Experiments

- A combination of pH and PVPP treatments can be used to remove many phenolics

- How does the removal of phenolics affect anodic fouling?
Areas for continuing research

- What is the fouling behavior of WSAE electrolysis after phenolics have been stripped? Hydrogen production?
- Regeneration of electrodes ($40 each pair)
- The efficiency of other fining agents such as activated carbon and gelatin
- Deadsorbing lignin molecules from PVPP
- What are some non-oxygen producing competing reactions? Is there a place to commercialize this?
- Improvements in the experimental system
Relatively Short-Term Research Objectives

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Questions?
Beaudry EG, Caro RF. Electrolysis of Weak Black Liquor and Bleach Effluent. 1996 Engineering Conference; September 16-19 1996; Chicago IL.


