Improving Hydrogen Efficiency During Thermochemical Conversion of Biomass to Fuels

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Overview

- Hydrogen Requirement in Thermochemical Biofuel Pathway
- Microbial Electrolysis Technology (MEC)
- Prevent Organic Carbon Loss via Aqueous Phase
- Potential to Improve Process Efficiency via Energy Recovery
- Address Separations and Unit Operations to Support MEC
- Discuss Potential for Carbon and Separations Efficiency Improvement in Bio-oil Pathways
Problem Statement

- Deoxygenation of biomass
- Need for hydrogen to make HC fuels
- Loss of carbon to aqueous phase

Goals

- Develop technology for hydrogen production in biorefinery to facilitate biomass deoxygenation.
- Reforming of aqueous phase organics to hydrogen via microbial electrolysis cell (MEC) technology.
**Microbial Electrolysis**

- Hydrogen production from pyrolysis-derived aqueous phase
  - Address aqueous carbon emulsified with oil phase – acidic and polar molecules
  - Causes instability of bio-oil
  - Corrosivity of bio-oil
- Carbon, Hydrogen and Separations Efficiency for Bio-oil Pathways program (CHASE)
- Microbial electrolysis
  - Conversion of bio-oil aqueous phase (BOAP) organics to hydrogen
  - Anode: Conversion of degradable organics to electrons, protons and CO₂
  - Cathode: Proton reduction to hydrogen at applied potential of 0.3-1V.
  - Uses electroactive biofilms capable of direct electron transfer

**Pathway: Bio-oil Aqueous Phase (BOAP)**

→ electrons + protons (anode)
→ H₂ (cathode)

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Integrated Pyrolysis-Microbial Electrolysis

Bio-oil production

Bio-oil production process scheme

- Feedstock: switchgrass
- Particle size: less than 2mm
- Water content of switchgrass: 7-8 wt%.
- Feeding rate: 10kg/hr
- Reaction temperature: 500°C
- Bio-oil: combined by three condensers
- Add water to bio-oil (4:1 ratio) to separate aqueous fraction.

Pilot auger pyrolysis reactor at UTK Center for Renewable Carbon

Products from switchgrass pyrolysis

<table>
<thead>
<tr>
<th></th>
<th>Bio-oil production (wt%)</th>
<th>Bio-oil yield (wt%)</th>
<th>Bio-char yield (wt%)</th>
<th>Non-condensable gas yield (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st batch</td>
<td></td>
<td>50</td>
<td>29</td>
<td>21</td>
</tr>
<tr>
<td>2nd batch</td>
<td></td>
<td>54</td>
<td>29</td>
<td>17</td>
</tr>
</tbody>
</table>

Production of bio-oil from switchgrass

## Bio-oil Aqueous Phase characterization...

<table>
<thead>
<tr>
<th>Classifications</th>
<th>Major compounds</th>
<th>Concentration in aqueous phase (g/L)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carboxylic acid</strong></td>
<td>Acetic acid</td>
<td>11.96</td>
<td>HPLC</td>
</tr>
<tr>
<td></td>
<td>Propionic acid</td>
<td>1.89</td>
<td>HPLC</td>
</tr>
<tr>
<td></td>
<td>Vanillic acid</td>
<td>2.69</td>
<td>HPLC</td>
</tr>
<tr>
<td><strong>Sugars</strong></td>
<td>Levoglucosan</td>
<td>15.33</td>
<td>HPLC</td>
</tr>
<tr>
<td><strong>Furans</strong></td>
<td>Furfural</td>
<td>1.01</td>
<td>HPLC</td>
</tr>
<tr>
<td></td>
<td>HMF</td>
<td>0.54</td>
<td>HPLC</td>
</tr>
<tr>
<td></td>
<td>2(5H)-Furanone</td>
<td>1.17</td>
<td>GC</td>
</tr>
<tr>
<td><strong>Alcohols</strong></td>
<td>1,3-propanediol</td>
<td>1.84</td>
<td>GC</td>
</tr>
<tr>
<td></td>
<td>1-hydroxybutanone</td>
<td>1.35</td>
<td>GC</td>
</tr>
<tr>
<td><strong>Aldehydes and ketones</strong></td>
<td>Cyclohexanone</td>
<td>0.07</td>
<td>GC</td>
</tr>
<tr>
<td></td>
<td>3-methyl-1,2-cyclopentanedione</td>
<td>0.46</td>
<td>GC</td>
</tr>
<tr>
<td><strong>Phenols and alkyl phenols</strong></td>
<td>1,2-benzendiol</td>
<td>1.77</td>
<td>HPLC</td>
</tr>
<tr>
<td></td>
<td>Phenol</td>
<td>1.8</td>
<td>HPLC</td>
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<tr>
<td></td>
<td>2-methoxyphenol</td>
<td>0.25</td>
<td>GC</td>
</tr>
<tr>
<td></td>
<td>2-methyl-4-methyphenol</td>
<td>0.07</td>
<td>GC</td>
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<tr>
<td></td>
<td>2,6-Dimethoxyphenol</td>
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<td>GC</td>
</tr>
<tr>
<td></td>
<td>3-ethylphenol</td>
<td>0.56</td>
<td>GC</td>
</tr>
<tr>
<td></td>
<td><strong>Sum</strong></td>
<td>43.01</td>
<td></td>
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</tbody>
</table>

Anode Biocatalyst Development

- Growth of electroactive biofilms for conversion of BOAP compounds.
- **Goals**
  - Tolerance to phenols and furan aldehydes
  - Optimize population diversity
- **Approach**
  - Use of optimized system (MFC) configuration
  - Use of previously optimized process parameters.

Successful development of anode biocatalyst for conversion of switchgrass bio-oil aqueous phase, including removal of acetic acid and phenolic acids.
MEC optimization is a complex process, requiring system design, process and biological parameter optimization.

**H₂ production from BOAP – Batch Run**

- 0.1 to 0.3 g/l batch BOAP
- 12-24 hour experiment

**Hydrogen Yield from Bio-oil Aqueous Phase**

- Anode Coulombic Efficiency (CE)
  - 0.1 g/l
  - 0.2 g/l
  - 0.3 g/l

- Cathode Efficiency
  - 0.1 g/l
  - 0.2 g/l
  - 0.3 g/l

**H₂ Productivity L/L-anode-day**

- 0%
- 20%
- 40%
- 60%
- 80%
- 100%

- 0.1 g/l
- 0.2 g/l
- 0.3 g/l

**Hydrogen Yield from Bio-oil Aqueous Phase**

H₂ production from BOAP – Continuous Run

- 2 g/l/d to 10 g/l/d continuous BOAP feed
- 12-24 hour experiment

Demonstrated an yield of hydrogen of ~ 80% from bio-oil aqueous phase.

Novelty of Bioelectrochemical Systems

1. Biological electron transfer and electroactive biofilm development
2. Biocatalysis/Electrocatalysis synergy
3. Diversification potential

<table>
<thead>
<tr>
<th>Type of BES</th>
<th>Cathode</th>
<th>Product</th>
</tr>
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<tbody>
<tr>
<td>BES</td>
<td>Oxygen</td>
<td>Electricity</td>
</tr>
<tr>
<td>MFC</td>
<td>Protons</td>
<td>Biohydrogen</td>
</tr>
<tr>
<td>MEC</td>
<td>Acetate</td>
<td>Ethanol/biofuel</td>
</tr>
<tr>
<td>BES</td>
<td>Oxygen</td>
<td>Hydrogen peroxide</td>
</tr>
<tr>
<td>BES</td>
<td>Carbon dioxide</td>
<td>Electrofuels</td>
</tr>
<tr>
<td>BES</td>
<td>other/sunlight</td>
<td>Photo/biofuels</td>
</tr>
</tbody>
</table>


MEC Supporting Tasks for Biorefinery Application

**Problem**

- Understanding of biooil composition
- Biooil pH, instability
- Hydrogen requirement

**Solutions**

- Produce bio-oil /characterize, analyze aqueous phase
- Microbial electrolysis of pyrolysis aqueous Phase
- Membrane separations Biocatalyst recovery and recycle
- Electrolysis cell materials

**Carbon, Hydrogen and Separations Efficiency along the complete pathway**

- GHG reduction
- Life cycle analysis Techno-economic Analysis
- Industry partners

**Upgraded Intermediate Distribution and Refining**

- Membrane process modules, supplies

**Feedstock Supply**

- Feedstock Processing and Handling

**Balance of Plant**

- Thermochemical Deconstruction
  - Methods can include:
    - Pyrolysis
    - Solvent Liquefaction
    - Gasification

- Intermediate Upgrading
  - Intermediates can include:
    - Bio-Oils
    - Gasous Mixture

- Distribution, Infrastructure, and End Use

**Supporting Tasks for Biorefinery Application**

- Membrane separations
- Biocatalyst recovery and recycle
- Microbial electrolysis of furanic and phenolic Substrates
- Electrolysis cell materials
- Industry partners
Potential for MECs in Algal Conversion Pathways

Without MECs

- Pretreatment & Conditioning
- Fermentation and distillation
- Lipid Extraction and Solvent Recovery
- Product Purification and Upgrading

With MECs

- Pretreatment & Conditioning
- Filtration
- Lipid Extraction and Solvent Recovery
- Product Purification and Upgrading

* Sustainability, Special Issue: Sustainability in Bioenergy Production, Borole, A. P., 2015, Sustainable and Efficient Pathways for Bioenergy Recovery from Low-value Process Streams via Bioelectrochemical Systems in Biorefineries." 7(9): 11713-11726.\*
Future Work

• Achieve performance to enable commercial consideration

• Scale up studies

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