Integrated Biological Hydrogen Production Research at Clemson University

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Introduction

• What is a biofuel?
  – Fuels produced from biomass sources
    • Biomass sources – agricultural byproducts and feedstocks, forestry wastes
  – Fuels produced by the action of microorganisms
Biorefinery Concept

- **Biorefinery** - a facility that uses biological, chemical and physical processing to produce biofuels, biopolymers and pharmaceuticals
- Biofuel compounds will primarily be economically feasible to produce in the context of a biorefinery
Solar water heaters and photobioreactors for algal oil and $H_2$ production

Bioproduction/biofuel processes

Biomass Feedstock

Biomanufacturing - Biorefinery Facility

Solar Energy

CO$_2$

Pharmaceuticals

Biochemicals

Biomaterials

Bioenergy
- Biodiesel
- Ethanol
- Hydrogen
- MFC electricity

Utilities
Biofuels Production

• Ethanol
  – Anaerobic fermentation of organic substrate by yeasts

• Hydrogen
  – Anaerobic fermentation of organic substrate by bacteria and archae

• Methane
  – Anaerobic fermentation of organic substrate by mixed cultures of bacteria and archae

• Biodiesel
  – Oils produced by terrestrial plants or algae are chemically converted (transesterified) to biodiesel

• Bioelectricity
  – Facultative oxidation of organic substrates to produce electron flow by bacteria
Common biomass sources

• Dedicated biomass – grown for biofuel production
  – Corn, wheat – starch sources
  – Sugarcane, sugar beet – sugar sources
  – Grasses (switchgrass) – cellulosic sources
• Agricultural residues – byproducts of food/fiber production
  – Crop processing wastes
    • sugarcane bagasse (sugarcane stalks)
    • corn stover (corn stalk residue)
  – Fruit/vegetable processing wastes
• Forestry residues – byproducts of timber production
• Animal manures
Biomass resources available in the US

Peach residues in SC

- 200 million pounds of peaches harvested yearly in SC, primarily for fresh market
- 20 million pounds discarded yearly, due to bruising, imperfections etc
- Currently, these cull peaches not processed to fruit juice or canned peaches
- Fresh peaches contain ~ 90% water, 10% sugars (sucrose, glucose, fructose)
How much biofuel produced?

• Primary biofuels produced currently in US
  – Ethanol from dedicated corn and corn stover
  – Biodiesel from terrestrial crops (soybean)

• Future predicted biofuels production
  – Ethanol from switchgrass, other cellulosics
  – Biodiesel from algal cultures
  – Hydrogen from variety of sources
World biodiesel and ethanol production and projections

Hydrogen gas

• Hydrogen viewed by DOE as future
• 95% of hydrogen currently is from fossil fuels
  – thermocatalytic conversion of natural gas- CH₄
• Hydrogen can be produced by splitting water
  – electrolysis – 2H₂0 →2H₂+ O₂
  – energy intensive; thermodynamically unfavorable
• Hydrogen can be produced biologically
  – fermentative bacteria and certain algae
Biological production of hydrogen

• Fermentation:
  – Certain bacteria can use carbohydrate and produce H₂ as byproduct
  – 4 mol H₂ and 2 mol acetate produced per mol glucose

\[
C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2
\]

• Hydrogen synthesis
  – inhibited by H₂ accumulation in headspace
  – Inhibited by pH values below 5
Biological production of hydrogen

- Glucose
  - ATP
  - ADP
  → Glucose-6-phosphate

- Fructose-6-phosphate
  - ATP
  - ADP

- Fructose 1,6-bisphosphate
  - ATP
  - ADP

- Glyceraldehyde-3-phosphate
  - NAD^+
  - Fd_{ox}
  - 2H^+
  - H_2
  - P, 1,3-diphosphoglycerate
  - ADP
  - ATP

- Phosphoenolpyruvate
  - ADP
  - ATP

- Pyruvate
  - CoA
  - Fd_{ox}
  - 2H^+
  - H_2

- Acetyl-CoA
  - ADP
  - ATP

- Acetyl-phosphate
  - ADP
  - ATP

- Acetate

- *Schroder: Arch Microbiol, 1994, 161, 460-470*
Biological production of hydrogen

- *Thermotoga neapolitana*
  - a hyperthermophilic bacterium first isolated from the bay of Naples, Italy
  - a gram-negative, rod-shaped, obligate anaerobic, fermentative extreme thermophiles surrounded by the bag-shaped sheath-like outer structure called “toga”
  - the optimal temperature is 77°C.
Experimental objectives

• Screen media for *Thermotoga neapolitana*
  – Glucose, sucrose, cellulose
  – Peach solids

• Optimize process:
  – pH control
  – Minimize nutrient addition
Methods

• Batch incubations
  – 5 g/L carbon source or 5 g/L peach solids (Redhaven, depitted, blended), 4 g/L nitrogen, nutrients, and salt added (saltwater microbe)
  – Media flushed with N₂ to remove O₂
  – Incubated at 77°C for 24 – 40 hours on orbital shaker bath
  – H₂ measured using gas chromatography
## Results – Screening carbon sources

<table>
<thead>
<tr>
<th>Carbon Sources</th>
<th>Percentage of hydrogen concentration (%)</th>
<th>Absolute total Pressure (kPa) at 25°C</th>
<th>Hydrogen concentration (mmol H₂/L medium)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>28.95</td>
<td>142</td>
<td>30.36ᵃ</td>
</tr>
<tr>
<td>Sucrose</td>
<td>26.41</td>
<td>141</td>
<td>27.42ᵇᵃ</td>
</tr>
<tr>
<td>Xylan</td>
<td>26.29</td>
<td>139</td>
<td>27.00ᵇᵇ</td>
</tr>
<tr>
<td>Rice</td>
<td>25.67</td>
<td>137</td>
<td>25.89ᵇᶜ</td>
</tr>
<tr>
<td>Cellobiose</td>
<td>24.80</td>
<td>128</td>
<td>23.49ᵇᶜ</td>
</tr>
<tr>
<td>Xylose</td>
<td>24.42</td>
<td>120</td>
<td>21.69ᶜ</td>
</tr>
<tr>
<td>Corn</td>
<td>23.40</td>
<td>129</td>
<td>22.26ᶜ</td>
</tr>
<tr>
<td>Starch</td>
<td>22.70</td>
<td>130</td>
<td>22.34ᶜ</td>
</tr>
<tr>
<td>Beet</td>
<td>14.96</td>
<td>108</td>
<td>11.94ᵈ</td>
</tr>
<tr>
<td>Cellulose</td>
<td>3.03</td>
<td>108</td>
<td>2.41ᵉ</td>
</tr>
</tbody>
</table>
Results – Peach media

• Similar $\text{H}_2$ yields for peach vs glucose media
• Autoclaving of media not necessary (energy savings)
• $\text{H}_2$ production rate very sensitive to pH
  – Optimum initial pH = 8
Projected impact

• 20 million lbs cull peaches per season
  – 8 g H₂ produced from 180 g sugar
  – 340 kg H₂/day could be produced during season

• Average home in US
  – Energy use = 10,900 kWh/yr (~ $1,000/yr @ $0.10/kWh)
  – Therefore, 1.25 kW H₂ fuel cell required
  – 1.68 kg H₂ needed per day to power 1.25 kW fuel cell

• ~ 200 homes could be powered by H₂ produced by fermentation of cull peaches during season

• Many other sugary wastes could be used for year-round operation
Next Phase Objectives

• Design pilot scale system
  – Use Sustainable Shed (model house)
  – Use solar water heater to heat water
  – Size PEM fuel cell to convert $\text{H}_2$ to electricity
Conclusions

• Exciting research on biofuels production is going on in Biosystems Engineering at Clemson!

• Contact me if questions
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  http://www.clemson.edu/agbioeng/bio/drapcho.htm
Questions?