Novel Process to Fractionate Algal Biomass into Fuels and Value Added Chemicals Using the Flexible Biorefinery Model.

Nick Nagle Lieve Laurens, Ryan Davis, Philip Pienkos and John McGowen

BIO PacRim
San Diego
December 8, 2014
Green = algae cell density
Harmonization Results: Year-Average (13.2 g/m²/day)

Updated baseline, $/GGE (2011$)
Biomass fractionation for fuels & value-added chemicals

- Carbohydrates
  - Fermentation
    - Ethanol
    - Succinic acid
    - Farnesene
  - Blend stocks
  - Aviation Fuel
  - Green Diesel
- Lipids
  - HDO/HI
    - Animal feed
    - Isobutanol
    - Bio-plastics
    - Methane
- Proteins
  - AD fermentation, etc
    - Animal feed
    - Isobutanol
    - Bio-plastics
    - Methane
Scheme for integrated algal biomass processing

<table>
<thead>
<tr>
<th>Fuel</th>
<th>HL NC</th>
<th>HL SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acids (FAME) (% DW)</td>
<td>57.3</td>
<td>38.6</td>
</tr>
<tr>
<td>Diesel equivalent (gallon/ton)</td>
<td>138.4</td>
<td>93.2</td>
</tr>
<tr>
<td>Fermentable Sugars (% DW)</td>
<td>10.9</td>
<td>39.4</td>
</tr>
<tr>
<td>Ethanol (gallon/ton)</td>
<td>13.8</td>
<td>59.0</td>
</tr>
<tr>
<td>Total fuel energy ($10^3$ Btu/ton)</td>
<td>18060</td>
<td>15965</td>
</tr>
<tr>
<td>Total GGE per ton biomass (GGE/ton)</td>
<td>155.6</td>
<td>137.5</td>
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</tbody>
</table>
Algal feedstock production at ASU

Using a Combination of PBR’s and Open Raceways

Three Production Strains:
- *Chlorella* sp.
- *Scenedesmus* sp.
- *Nannochloropsis* sp.

Three Growth Regimes:
- High Protein (Early)
- High Carbohydrate (Mid)
- High Lipid (Late)
Feedstock Composition and Rates of Lipid Accumulation

*Chlorella* sp.
*Scenedesmus* sp.
*Nannochloropsis* sp.

Early (high protein)
Mid (high carbohydrate)
Late (high lipid)
Dilute-acid pretreatment to release lipid & carbohydrate

- CEM Explorer Microwave Reactor
- Automated system w/36-positions
- 300 watt output
- Stir bar mixing
- Rapid heating

- Central Composite Design

- Track both fatty acid and carbohydrate release

Acid

Temperature

145 ºC, 2% H₂SO₄
Response of lipid recovery from different strains

<table>
<thead>
<tr>
<th>Element</th>
<th>HL CZ</th>
<th>HC CZ</th>
<th>HL SD</th>
<th>HC SD</th>
<th>HL NC</th>
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</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>76.83</td>
<td>77.42</td>
<td>77.53</td>
<td>76.61</td>
<td>76.87</td>
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<tr>
<td>Hydrogen</td>
<td>11.74</td>
<td>11.54</td>
<td>12.00</td>
<td>11.91</td>
<td>11.77</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.04</td>
<td>0.05</td>
<td>0.03</td>
<td>0.10</td>
<td>0.09</td>
</tr>
<tr>
<td>Oxygen</td>
<td>11.86</td>
<td>11.37</td>
<td>11.04</td>
<td>11.93</td>
<td>11.96</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.004</td>
<td>0.006</td>
<td>0.005</td>
<td>0.026</td>
<td>0.036</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>0.039</td>
</tr>
</tbody>
</table>
Response of carbohydrate recovery from different strains

<table>
<thead>
<tr>
<th>Microalgae</th>
<th>Glucose</th>
<th>Galactose/Rhamnose</th>
<th>Mannose</th>
</tr>
</thead>
<tbody>
<tr>
<td>% (based on total carb)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCNC</td>
<td>69.6</td>
<td>21.4</td>
<td>8.9</td>
</tr>
<tr>
<td>HLNC</td>
<td>72.5</td>
<td>18.3</td>
<td>9.2</td>
</tr>
<tr>
<td>HCCZ</td>
<td>80.1</td>
<td>17.0</td>
<td>2.9</td>
</tr>
<tr>
<td>HLCZ</td>
<td>84.9</td>
<td>12.1</td>
<td>3.0</td>
</tr>
<tr>
<td>HCSD</td>
<td>81.7</td>
<td>3.8</td>
<td>14.5</td>
</tr>
<tr>
<td>HLSD</td>
<td>75.9</td>
<td>3.3</td>
<td>20.8</td>
</tr>
</tbody>
</table>

NC: Laminarin  
CZ: Starch  
SD: Glucomannan
Energy yield from integrated algal biomass processing

<table>
<thead>
<tr>
<th></th>
<th>SD</th>
<th>CZ</th>
<th>NC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gasoline equivalent</strong> (gal/ton)**</td>
<td>34</td>
<td>27</td>
<td>23</td>
</tr>
<tr>
<td><strong>Btu equivalent</strong> (x10e3)</td>
<td>3959</td>
<td>3156</td>
<td>2700</td>
</tr>
<tr>
<td><strong>Diesel equivalent</strong> (gal/ton)</td>
<td>37</td>
<td>84</td>
<td>50</td>
</tr>
<tr>
<td><strong>Btu equivalent</strong> (x10e3)</td>
<td>4541</td>
<td>10311</td>
<td>6171</td>
</tr>
<tr>
<td><strong>Total fuel energy</strong> (x10e3 Btu/ton)</td>
<td>8500</td>
<td>13467</td>
<td>8871</td>
</tr>
<tr>
<td><strong>Total GGE</strong> (GGE/ ton)</td>
<td>73</td>
<td>116</td>
<td>76</td>
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</tbody>
</table>
Fermentation of Algal Sugars by Yeast

**HC SD**

- Early stage
- Mid stage
- Late stage

**HC CZ**

- Early stage
- Mid stage
- Late stage

Ethanol yield (%) vs. time (hr)
Hydrodeoxygenation (HDO) of Algae Oil

Before

After

HL Chlorella DO
450 °C, 1300 psi H₂
5% Pd/C
LHSV = 1 hr⁻¹

H₂ Consumption
CO Production
CO₂ Production

Time on Stream (h)

HL Chlorella DO
1300 psi H₂, 450 °C

GC Area %

Soybean Oil HDO
1300 psi H₂, 450 °C

Unidentified
Aromatic
i-paraffin
n-paraffin
Naphthenes

n-paraffin
65%
12%
10%
1%

n-paraffin
75%
8%
10%
3%
Potential Cost Savings from Fractionation Process

Productivity
13 g m² day⁻¹

30 g m² day⁻¹

50 g m² day⁻¹

Fuel Yield
Harmonization baseline
Fractionation process
Conclusions

• Integrated microalgae biomass processing is able to recovery lipids and fermentable sugar.
• Acid concentration and temperature have combined effects for lipids and sugar recovery.
• The response of microalgae biomass to pretreatment is strain-dependent
• Achieve >100 GGE/ton for the late harvest *Scenedesmus* sp. and *Nannochloropsis* sp. strains.
• Algal lipids can be catalytically to hydrocarbons with no added processing
• Addition of ethanol as coproduct can significantly improve process economics
# Acknowledgments

<table>
<thead>
<tr>
<th>NREL</th>
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<tbody>
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Note: The logos for NREL and ASU are displayed at the bottom of the page.
Thank you.
Any questions?