Algae Under Pressure and in Hot Water – Hydrothermal Pathways to Renewable Fuels

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society transitions to new energy sources when it improves life - not because of scarcity
Why Liquid Fuels from Biomass?

~ 15 TW  
~ 450 quads

We need liquid fuels for transportation.

Biomass is recently stored solar energy - **renewable energy**

We can grow enough biomass to meet this need.

Biofuels are renewable - live off the sun in real time.
Can algae be a better biofuel feedstock?

- Major issues with terrestrial crops:
  - Expensive
  - Food/Feed vs. fuel
  - Require lots of land, water, and fertilizer
  - Less efficient at photosynthesis
  - Indirect land use change

<table>
<thead>
<tr>
<th>Crop</th>
<th>Oil Yield (L ha⁻¹ y⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybean</td>
<td>450</td>
</tr>
<tr>
<td>Camelina</td>
<td>560</td>
</tr>
<tr>
<td>Sunflower</td>
<td>955</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>1,190</td>
</tr>
<tr>
<td>Jatropha</td>
<td>1,890</td>
</tr>
<tr>
<td>Oil Palm</td>
<td>5,950</td>
</tr>
<tr>
<td>Microalgae</td>
<td>3,800-50,800</td>
</tr>
</tbody>
</table>

Microalgae

- Aquatic biomass (lots of water)
- Can have very high oil content
  - along with protein and polysaccharide
- No food vs. fuel competition
- Water provides structural support (no lignin)
- High biomass growth rates
  - ~ 5000 gal/acre/yr (~ 10X relative to terrestrial biomass)
- Can grow in salt water (reduce fresh water needed)
- Industrial ecology possibilities - co-locate with water treatment and coal-fired power plants
Algae need much less land than conventional energy crops!

Land Area to Replace 50% of Petroleum Distillates

Adapted from Bryan, et al. (2008)
Going REALLY green: World's first bio-building powered by ALGAE opens in Hamburg
Biofuel from Microalgae

Standard approach is dewatering, drying, lipid extraction (e.g., with hexane), and oil processing to make biodiesel or "green" diesel

- $$\text{\$\$\$\$}$, requires organic solvents, acids, bases
- Let’s use a potentially greener approach!
Overview

- Develop biofuel processes that use wet algae paste
  - avoid drying
  - minimal dewatering
  - no lipid extraction

- Feedstock flexible
  - high-lipid algae not required
  - useful for other wet biomass

- Hydrothermal approach - Use high-temperature liquid water to convert biomass into fuels
  - mimic nature
  - break down biomacromolecules in algae
Introduction to High-Temperature Water (HTW)

HTW: Liquid H$_2$O at 200 – 350°C ($T_C = 374°C$)

Properties of HTW different from room-temperature water

• Fewer and less persistent H-bonds
• Lower dielectric constant
  $\rightarrow$ Increased solubility of organic compounds
• Higher $K_W = (H^+)(OH^-)$
  $\rightarrow$ enhanced acid catalysis

![Graph showing log $K_W$ vs. temperature (°C)]
Hydrothermal Routes from Wet Algae to Biofuels

Wet Biomass (algae) → Liquefaction (350 °C) → Crude Bio-oil

- Carbonization (~200 °C)
- Gasification (~600 °C)
- Esterification (Solvothermal)
- Deoxygenation
- Upgraded

Wet Biomass (algae) → Crude Bio-oil → Crude Biodiesel

- ~350 °C
- CH₄, H₂

Processes that work with wet biomass (its natural state) and avoid organic solvents could be less costly, more energy efficient, and more environmentally sustainable.

Savage, Science, 2012
Microalgae HTL Process

Microalgae Growth

CO₂
H₂O
aqueous by-product

Energy Recovery

Hydrothermal Liquefaction (HTL)

bio-oil components

Energy Recovery

Hydrothermal Catalytic Processing

N, P recycling

Recover energy & nutrients in aqueous stream – essential for energy-positive & sustainable process

OIL

liquid fuel
Hydrothermal Liquefaction of Microalgae

Valdez et al., *Biomass & Bioenergy*, 2012
Experimental Procedure

HTL Products

Aqueous Phase

Biocrude (Organic Phase)

Light Biocrude

Heavy Biocrude

Solids

Pressure (MPa)

Temperature (°C)

Liquid Water

Water Vapor

0 5 10 15 20 25 30

100 200 300 400 500

250°C 300°C 350°C 400°C
## Elemental Analysis of Bio-Crude

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Algae</td>
<td>43.3</td>
<td>6.0</td>
<td>25.1</td>
<td>6.4</td>
<td>0.53</td>
</tr>
<tr>
<td>200</td>
<td>74.6</td>
<td>10.8</td>
<td>11.8</td>
<td>2.4</td>
<td>0.44</td>
</tr>
<tr>
<td>300</td>
<td>75.2</td>
<td>10.3</td>
<td>9.8</td>
<td>4.3</td>
<td>0.79</td>
</tr>
<tr>
<td>400</td>
<td>76.7</td>
<td>10.3</td>
<td>8.7</td>
<td>3.6</td>
<td>0.91</td>
</tr>
<tr>
<td>Crude Oil(^2)</td>
<td>83-87</td>
<td>10-14</td>
<td>0.1-1.5</td>
<td>0.1-2.0</td>
<td>0.5-6.0</td>
</tr>
</tbody>
</table>

From Brown, Duan, & Savage., *Energy & Fuels*. 2010

- O decreased with temp.
- S increased with temp.

\(^2\)Data from http://en.citizenendum.org/wiki/Petroleum

\(\text{Nannochloropsis sp.}\)
Biocrude Yields (wt%) from Isothermal HTL

Valdez et al., Biomass & Bioenergy, 2012

50 – 80% energy recovery in biocrude
Total Ion Chromatogram of Bio-Crude

350 °C, 60 min

C16 fatty acids
C & N distributions at 20 min

250°C

C

N

350°C

400°C

Light Biocrude

Heavy Biocrude

Water-soluble Products

Solids

Gas

Light Biocrude

Heavy Biocrude

Water-soluble Products

Solids

Light Biocrude

Heavy Biocrude

Water-soluble Products

Solids

Light Biocrude

Heavy Biocrude

Water-soluble Products

Solids
Reactions of Intermediate Products

350°C, 40min
15 wt % slurry

200mL Induction-heated Parr Reactor

→

Solids

→

Aqueous-phase Products

→

Light Biocrude

→

Heavy Biocrude + Gas

→

350°C, 10-40min
5 wt % loading

→

Product Workup

→

4mL Swagelok Reactor
Reaction of Aqueous-phase Products

- Aqueous-phase produces Light and Heavy Biocrudes and relatively large amounts of CO₂ (~3 wt %)

Valdez & Savage, *Algal Research*, under review
Reaction of Light Biocrude

- Light Biocrude produces Aqueous-phase and Heavy Biocrude
Reaction of Heavy Biocrude

- Heavy Biocrude produces Aqueous-phase products, Light Biocrude and $H_2$, $C_1$, and $C_2$ gases

Valdez & Savage, *Algal Research*, under review
Building a Kinetics Model

- Write & solve governing equations
  - \( x_i \) = mass fraction of each product
  - 1\textsuperscript{st} order kinetics

- Estimate rate constants by minimizing objective function

\[
\text{Objective Function} = \sum_i \left( x_i^{\text{exp.}} - x_i^{\text{calc.}} \right)^2
\]

- Used MATLAB, Constrained, non-linear multivariable function
Model & Exptl. Results for HTL

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**250°C**
- Solids
- Aqueous-phase Products
- Heavy Biocrude
- Light Biocrude
- Gas

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**300°C**
- Solids
- Aqueous-phase Products
- Heavy Biocrude
- Light Biocrude
- Gas

---

**350°C**
- Solids
- Aqueous-phase Products
- Heavy Biocrude
- Light Biocrude
- Gas

---

**400°C**
- Solids
- Aqueous-phase Products
- Heavy Biocrude
- Light Biocrude
- Gas
Biocrude yields from liquefaction of *Nannochloropsis* sp. at 60 min

Gas yields from hydrothermal treatment of *Nannochloropsis* sp. at 60 min

Model Predictions

High temp, short time gives highest biocrude yields

Rapidly heat to high temperature

“Fast” liquefaction

Fast Hydrothermal Liquefaction

- *Nannochloropsis sp.*
- 1.5 mL stainless steel batch reactors
- Thermocouple dummy reactors
- Setpoint temperatures 300-600°C
- Reaction times 1, 3, 5 min
- Quench in cold water
Temperature Profile

Temperature (°C) vs. Time (minutes)

- 600°C Setpoint Temperature: 593 °C
- 300°C Setpoint Temperature: 297 °C

Temperature Points:
- 176 °C
- 283 °C
- 297 °C
- 565 °C
- 593 °C
Total Biocrude Yield (wt.%)
Total Biocrude Yields - 1 minute

Reaction Ordinate

- Severity index that combines effects of time and temperature\(^1\)

\[
R_0 = \int_0^t \exp \left( \frac{T(t)\degree C - 100\degree C}{14.75\degree C} \right) \, dt
\]

- Used previously with wood pulping
- Numerical integration using experimental temperature trajectory

Total Biocrude Yield with $R_0$

Conv. HTL Data from Valdez et al., *Biomass and Bioenergy*, 2012
Biocrude O/C, N/C Ratios

Algae O/C = 0.353

Algae N/C = 0.145

Fast HTL O/C
Conv HTL O/C
Fast HTL N/C
Conv HTL N/C

Model Compound Approach

- Chemical details likely to be obscured starting with algae directly

How do model compounds react individually and interact with each other in HTW?
Phenylalanine

\[
\text{\begin{array}{c}
\text{NH}_2 \\
\text{COOH}
\end{array}}
\]

Protein

Ethyl Oleate

\[
\text{\begin{array}{c}
\text{O} \\
\text{O}
\end{array}}
\]

Lipids
Phenylalanine Reaction Pathway

[Changi et al., ChemSUSChem (2012)]
Ethyl Oleate Hydrolysis

- Sigmoidal shape - autocatalysis
- Adding oleic acid increases conversion
- Catalysis by product (oleic acid) confirmed

**Effect of Added Oleic Acid**

<table>
<thead>
<tr>
<th>Moles Oleic Acid</th>
<th>Conversion (240°C, 30 minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles Ethyl Oleate</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.07 ± 0.03</td>
</tr>
<tr>
<td>0.25</td>
<td>0.27 ± 0.07</td>
</tr>
<tr>
<td>0.5</td>
<td>0.41 ± 0.05</td>
</tr>
<tr>
<td>1</td>
<td>0.61 ± 0.09</td>
</tr>
</tbody>
</table>

Phenylalanine + Ethyl Oleate
Effect of Adding Ethyl Oleate

- Phenylethylamine (primary product) yield decreases with added ester
- Styrene, 2-phenylethanol (2° products) yields increase with added ester

Reactions enhanced in presence of ester

[Changi et al., ChemSUSChem (2012)]
Effect of Adding Phenylalanine

- Formation of new products - oleic acid amides, phenylacetaldehyde

\[
\text{N-phenylethyl-9-octadecenamide}
\]

At 350 °C and 10 min

[Changi et al., ChemSUSChem (2012)]
Reaction Network for Binary System

[Changi et al., ChemSUSChem (2012)]
Increased Rates

[Changi et al., ChemSUSChem (2012)]
Parity Plot for Binary System

- $C_{\text{exp}}$ (mol/L) vs. $C_{\text{model}}$ (mol/L)
- Data points for phenylethylamine, styrene, phenylethanol, and N-phenylethyl-9-octadecenamide.

University of Michigan
Insights to Chemistry of Algae Liquefaction

• Oligomerization in amino acid system at high temperatures
  – Decreases quality of bio-oil
  – Use hydrogenation strategy to prevent oligomers

• Binary mixtures of amino acids and esters form amides
  – Decreases yield of fatty acid components in bio-oil
  – Adds nitrogen to crude bio-oil
  – Rates of individual reactions increase
Summary

• Hydrothermal Liquefaction (HTL) converts wet biomass into crude bio-oil

• Reaction network for HTL of algae established
  – Reaction modeling, reactor engineering

• Fast HTL produces biocrude in higher yield and shorter time than conventional HTL
  – 66 wt.% yield in 1 min.

• Reaction ordinate unifies results from conventional and fast HTL

• Model compounds provide insights into HTL chemistry
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