Hydrothermal Liquefaction of Low-Lipid Microalgae to Produce Bio-crude Oil

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Outline

I Introduction

II Materials & Methodology

III Results & Discussions

IV Summary & Recommendations
Fossil fuels are non-renewable resources. We are luckily living in the “oil age”.

Adapted from the lecture slides from Prof. Stephen Marshak
Global Climate Change

IPCC, Climate Change 2007 Synthesis Report
Alternative Energy

Generate electricity and heat:

- Solar energy
- Wind farm
- Geothermal energy
- Hydroelectric power

Generate transportation fuel:

Biomass → Conversion → Biofuel

Renewable resources
Energy Consumption in the U.S.

How can we economically scale up the biofuel production in the future?

Biofuel production should not sacrifice environment quality.
Why Microalgae?

- Microalgae have faster growth rates, shorter growing cycles and higher photosynthetic efficiencies than terrestrial biomass.
- Algae production has LESS impact on current land-use for food production system.

Raceway Pond

Photobioreactor
Why Low-Lipid Microalgae?

Current algae-to-biofuel approach: Utilizing high-lipid microalgae to produce biodiesel.

Energy intensive (~75% of total)

Low-lipid algae grow faster than high-lipid algae.
Why Low Lipid Microalgae? (cont.)

- For the majority of algae species, high lipid content is obtainable only by sacrificing biomass production, and thus causes a net reduction in lipid productivity (Sheehan et al., 1998).

- Algae grown in wastewater and environmental algae blooms have lower lipid contents; and it is much more difficult to control the culturing conditions to encourage lipid production.
E²-Energy integrates algal growth for wastewater treatment with HTL of algal biomass, and provides synergistic recycling of carbon dioxide and the nutrients from HTL products to support multiple stages of algae production and biofuel conversion.

http://www.e2-energy.illinois.edu/
Comparison of Thermochemical Conversion (TCC) Technologies

Cons:
- High operating pressure
- Oil is unstable and needs upgrade
- Complex in reaction mechanisms and kinetics

Pros:
- Suitable for high-moisture feedstocks
- Similar to crude oil thus easier to incorporate into existing infrastructure
- Bio-crude oil has higher energy density than bio-crude oil produced from pyrolysis

Hydrothermal Liquefaction (HTL)

Pyrolysis

Gasification
Literature Review on HTL of Algae

- Most of the previous literature focused on high-lipid algae and overlooked fast-growing, low-lipid algae.
- A few studies investigated effects of heterogeneous catalyst.
- Elemental and energy balance of HTL were not discussed comprehensively.
- Reaction mechanisms and kinetics of HTL of low-lipid microalgae were NOT discussed in the literature.
Goal of This Study

To develop a viable technology to convert fast-growing, low-lipid content microalgae into bio-crude oil via hydrothermal liquefaction (HTL) process.
Objectives

- Determine appropriate low-lipid content algal species for HTL study by screening available algal species.

- Investigate the effects of operating conditions of HTL on product yields and bio-crude oil quality.

- Examine the effects of catalysts and conduct preliminary evaluation of the selected catalysts based on the conversion efficiency and bio-crude oil quality.

- Analyze the elemental distribution and energy balance of HTL process.

- Characterize HTL products to better understand reaction pathways in HTL process.

- Explore the reaction kinetics and mechanisms of HTL of microalgae.
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HTL Process

- **Microalgae**
  - 20-30% Solid content

- **Reactor**

- **Nitrogen**
  - Residual air

- **Gas product**

- **Aqueous product**

- **Bio-crude oil**

- **Solid Residue**

- **Temperature was controlled and held for a certain time (retention time)**

Raw oil
HTL Products Recovery Procedure

Feedstock

Hydrothermal Liquefaction

Reaction Mixture

Filtration

Water Insoluble

Moisture Measurement

Raw Oil

Aqueous Product 2

Aqueous Product 1

Toluene Extraction

Gas Product

Bio-crude Oil

Solid Residue

Aqueous Product
Temperature & Pressure in a Typical HTL Test

![Graph showing temperature and pressure over time during a HTL test. The graph includes labels for heating, reaction time, and cooling stages.]
Experimental Design

- **Effect of operating parameters**
  - Reaction temperature (100°C - 300°C)
  - Retention time (0-120 min at five temperature levels)
  - Initial pressure of N₂ (0-100 psi or 0-0.69 MPa, gauge pressure)

- **Effect of catalysts**
  - Heterogeneous catalysts
    - Pd/Al₂O₃, Pd/C, Pt/Al₂O₃, Pt/C, Raney Ni (Al-Ni 50 wt%-50 wt%)
    - How can the catalysts be changed after HTL? (ESEM)
  - Homogeneous catalysts
    - NaOH, Na₂CO₃
Experimental Design (cont.)

- Elemental and energy balance of HTL
  - Elemental Balance
    - Elemental composition (C, H, N and O)
    - Carbon recovery (CR)
    - Nitrogen recovery (NR)
  - Energy Balance
    - Energy recovery (ER)
    - Energy consumption ratio (ECR)

- Characterizations of HTL products
  - Bio-crude oil (Composition, boiling point, heating value)
  - Water-soluble organic compounds
  - Gaseous product composition
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Screening Algal Species for HTL
Bio-crude Oil Yield & Lipid Content of Different Feedstocks

- Relatively high bio-crude oil yield and low-lipid content.
- High toluene solubility of raw oil product—easily to be upgraded into transportation fuel.
- Availability of algal feedstock (large amount of feedstock is needed for HTL tests).
Contents of Ash and Protein vs. Oil Quality

Higher protein content indicates better oil quality (higher solvent-soluble fraction).

*Chlorella pyrenoidosa* (green microalgae) and *Spirulina platensis* (cyanobacteria) were chosen as the representative low-lipid content algal species.
### Characteristics of Algal Species

*Chlorella pyrenoidosa* (green microalgae) and *Spirulina platensis* (cyanobacteria) were chosen as the representative low-lipid content algal species.

<table>
<thead>
<tr>
<th>Properties</th>
<th>C. pyrenoidosa</th>
<th>S. platensis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (wt %)&lt;sup&gt;[a]&lt;/sup&gt;</td>
<td>6.3</td>
<td>6.5</td>
</tr>
<tr>
<td>Dry solid content (wt %)&lt;sup&gt;[a]&lt;/sup&gt;</td>
<td>93.7</td>
<td>93.5</td>
</tr>
<tr>
<td>Volatile solid content</td>
<td>94.4</td>
<td>90.5</td>
</tr>
<tr>
<td>Ash content</td>
<td>5.6</td>
<td>9.5</td>
</tr>
</tbody>
</table>

#### Chemical composition

<table>
<thead>
<tr>
<th></th>
<th>C. pyrenoidosa</th>
<th>S. platensis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude protein</td>
<td>71.3</td>
<td>64.4</td>
</tr>
<tr>
<td>Crude fat</td>
<td>0.1</td>
<td>5.1</td>
</tr>
<tr>
<td>Acid detergent fiber</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Neutral detergent fiber</td>
<td>1.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Lignin</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Non-fibrous carbohydrate&lt;sup&gt;[b]&lt;/sup&gt;</td>
<td>22.0</td>
<td>18.9</td>
</tr>
</tbody>
</table>

#### Elemental composition

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O&lt;sup&gt;[b]&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>51.4</td>
<td>6.6</td>
<td>11.1</td>
<td>30.9</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O&lt;sup&gt;[b]&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>[a]</sup> On the total weight basis; <sup>[b]</sup> Calculated by difference
Effect of Operating Parameters on HTL Product Yields
Effect of Reaction Temperature

Chlorella

Product Yields (%)

Reaction Temperature (°C)

Bio-crude oil
Aqueous product
Gas product
Solid residue
Effect of Retention Time

- Bio-crude oil yield increased and solid residue yield decreased with retention time at different temperature levels.
- Retention time has a higher effect at low temperatures than at high temperatures.
Toluene solubility of raw oil increased with retention time and intended to plateau when the retention time was longer than one hour at high temperature levels.
Standard deviations of the product yields at different initial pressure were all below 2%. Different initial pressure had negligible effect on HTL product yields.
Effect of Catalysts on
HTL Product Yields
Effects of catalysts on bio-crude oil yield were more substantial at 280°C than at 240°C.

The highest bio-crude oil increase was about 10% with addition of catalysts.
Simulated Boiling Point Distribution of Bio-crude oil

With the increase of reaction temperature, the BP distribution of bio-crude oil shifted to the low temperature range, which indicates the oil quality was improved.
At 240°C, catalysts improved oil quality in term of increasing the fraction of molecules with low BP.

Heterogeneous catalyst had small effect on BP distribution at 280°C, while alkaline catalysts made the bio-crude oil BP distribution shift to the high temperature range.

Catalytic treatment of bio-crude oil with metal catalysts after HTL could be more effective.
Morphology Change of Catalysts after HTL

Original Pt/C

Unreacted algae

Chlorella, 240°C

Chlorella, 280°C

Minerals mixing
Morphology Change of Catalysts (Cont.)

Spirulina, 240°C
Pd/Al₂O₃

Spirulina, 280°C
Pd/Al₂O₃

Energy (Kev)

Carbon Deposition

Minerals mixing
Elemental and Energy Balance of HTL
Elemental Balance of the HTL Process

Carbon Recovery of Product (%) = \[
\frac{C\% \text{ of the product} \times \text{mass of product}}{\text{mass of carbon in dry matter of algae}} \times 100
\]

Nitrogen Recovery of Product (%) = \[
\frac{N\% \text{ of the product} \times \text{mass of product}}{\text{mass of nitrogen in dry matter of algae}} \times 100
\]
Energy Balance of the HTL Process

- Higher Heating Value (HHV):
  \[ \text{HHV} (\text{MJ} \cdot \text{kg}^{-1}) = 0.3383C + 1.422\left( H - \frac{0}{8} \right) \]

- Energy Recovery (ER):
  \[
  \text{Energy Recovery of Biocrude oil} \,(\%) = \frac{\text{HHV of biocrude oil} \times \text{mass of biocrude oil}}{\text{HHV of dry algae} \times \text{mass of dry algae}} \times 100
  \]

- Energy Consumption Ratio (ECR):
  \[
  \text{ECR} = \frac{\left[ w_i C_{pw} (T - T_{ini}) + (1 - w_i) C_{ps} (T - T_{ini}) \right] \cdot [1 - r_h]}{Y_{bio} \cdot \text{HHV}_{bio} \cdot (1 - w_i) \cdot r_c}
  \]

  *Energy consumed in the HTL process*

  *Energy recovered through combusting bio-crude oil*
As temperature increased, carbon was preferentially accumulated in the bio-crude oil.

About 40% of carbon in the feedstock remained in the aqueous product after HTL.
Some acids were produced first in the HTL process and then decomposed (some free hydrogen ions were produced and then consumed).

Addition of hydrogen to the oil product occurred at high temperatures.
As retention time increased, CR of bio-crude oil increased. Meanwhile, CR of solid residue decreased.
At 240°C, addition of alkaline catalysts decreased the CR of solid residue.

At 280°C, additions of metal and alkaline catalysts both decreased the CR of solid residue.

CR of bio-crude oil increased with addition of catalysts mainly due to the increase of its yield.
As temperature increased, more nitrogen was recovered by aqueous product.

NR of bio-crude oil increased mainly due to the increase of its yield.

About 75% of nitrogen remained in the aqueous phase after HTL.
As retention time increased, NR of bio-crude oil increased. Meanwhile, NR of solid residue decreased.
At 240°C, addition of alkaline catalysts decreased the NR of solid residue.

At 280°C, additions of metal and alkaline catalysts both decreased the NR of solid residue.
Bio-crude oil recovered more energy at high temperature with long retention time.

The highest ER of bio-crude oil was 65.4% at 280°C with 120 minutes retention time.
ECR decreased with reaction temperature increasing, which indicates HTL became more energetically favorable at higher temperature.

ECR increased with moisture content of feedstock. When moisture content of algal feedstock is more than 93%, ECR value exceeds 1.0.
Characterization of HTL Product & Reaction Mechanisms and Kinetics
Organic Compounds in Bio-crude Oil

Composition of bio-crude oil was very complicated.

Information from GC-MS spectra was too preliminary to derive the reaction mechanisms.

<table>
<thead>
<tr>
<th>No.</th>
<th>Retention time (min)</th>
<th>Compound</th>
<th>Area (%)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.32</td>
<td>Pyrazine, 2,5-dimethyl-</td>
<td>0.55</td>
<td><img src="image1.png" alt="Pyrazine 2,5-dimethyl" /></td>
</tr>
<tr>
<td>2</td>
<td>10.45</td>
<td>Benzaldehyde</td>
<td>0.57</td>
<td><img src="image2.png" alt="Benzaldehyde" /></td>
</tr>
<tr>
<td>3</td>
<td>11.50</td>
<td>Phenol</td>
<td>1.35</td>
<td><img src="image3.png" alt="Phenol" /></td>
</tr>
<tr>
<td>4</td>
<td>11.65</td>
<td>Pyrazine, 2-ethyl-6-methyl-</td>
<td>0.77</td>
<td><img src="image4.png" alt="Pyrazine 2-ethyl-6-methyl" /></td>
</tr>
<tr>
<td>5</td>
<td>14.19</td>
<td>Pyrazine, 3-ethyl-2,5-dimethyl-</td>
<td>0.99</td>
<td><img src="image5.png" alt="Pyrazine 3-ethyl-2,5-dimethyl" /></td>
</tr>
<tr>
<td>6</td>
<td>16.02</td>
<td>N-(3-Methylbutyl)acetamide</td>
<td>1.17</td>
<td><img src="image6.png" alt="N-(3-Methylbutyl)acetamide" /></td>
</tr>
<tr>
<td>7</td>
<td>20.35</td>
<td>Indole</td>
<td>1.76</td>
<td><img src="image7.png" alt="Indole" /></td>
</tr>
<tr>
<td>8</td>
<td>22.45</td>
<td>N-[2-Hydroxyethyl]succinimide</td>
<td>1.84</td>
<td><img src="image8.png" alt="N-[2-Hydroxyethyl]succinimide" /></td>
</tr>
<tr>
<td>9</td>
<td>22.69</td>
<td>1H-Indole, 4-methyl-</td>
<td>0.97</td>
<td><img src="image9.png" alt="1H-Indole, 4-methyl" /></td>
</tr>
<tr>
<td>10</td>
<td>24.95</td>
<td>Benzonitrile, 2,4,6-trimethyl-</td>
<td>0.96</td>
<td><img src="image10.png" alt="Benzonitrile, 2,4,6-trimethyl" /></td>
</tr>
</tbody>
</table>
Major Compound Classes in Bio-crude Oil

- **Hydrocarbons**
  - straight and branched hydrocarbon

- **Organic acids**
  - fatty acids
  - organic acids

- **Cyclic oxygenates**
  - phenols
  - phenol derivatives

- **Straight and branched amides**

- **Nitrogen and oxygen heterocyclic compounds**
  - pyrazine
  - pyrolle
  - indole
  - piperazinedione
  - derivatives of pyrrolidine and etc.
Effect of Reaction Temperature

Bio-crude oil from Chlorella

- Fractions of hydrocarbons, cyclic oxygenates and heterocyclic compounds increased with temperature.
- Fraction of organic acids decreased with reaction temperature.
Effect of Retention Time

- Fractions of organic acids decreased with retention time.
- Fractions of N&O heterocyclic compounds, and amides increased with retention time.
Fractions of amino acids (glycine and alanine) decreased with retention time.

Intermediates produced from protein hydrolysis were not stable under hydrothermal conditions.
Effect of Catalysts

At 240°C, addition of alkaline catalysts largely increased the fraction of N&O heterocyclic compounds and the fraction of organic acids were substantially decreased.

Effects of heterogeneous catalysts at 280°C were less pronounced.
Reaction Kinetics Model

HTL reaction can be simplified as:

Microalgae → Bio-crude oil + Aqueous product + Gas + Solid residue

\( \alpha \) is defined as the percent conversion of microalgae:

\[
\alpha = \frac{(m_t - m_{ini})}{m_{ini}}
\]

\( m_t \): Sum of CR of bio-crude oil, aqueous product and gas at a given retention time \( t \);

\( m_{ini} \): Sum of CR of bio-crude oil, aqueous product and gas at zero retention time

The apparent reaction kinetics can be derived by assumption of reaction order (1\(^{st}\) order reaction) and using Arrhenius equation:

\[
\ln \left[ \frac{1}{1 - \alpha} \right] = kt
\]

\[
k = A \exp \left( \frac{-E_a}{RT} \right)
\]

\[
\ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A
\]
Reactivity Kinetics Parameters

Reaction rate constants at different temperatures (Chlorella)

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>k (s⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.0000798552</td>
<td>0.98</td>
</tr>
<tr>
<td>220</td>
<td>0.0001274990</td>
<td>0.93</td>
</tr>
<tr>
<td>240</td>
<td>0.0001552200</td>
<td>0.89</td>
</tr>
<tr>
<td>260</td>
<td>0.0001580119</td>
<td>0.96</td>
</tr>
<tr>
<td>280</td>
<td>0.0002831621</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Apparent kinetic parameters for HTL of microalgae

<table>
<thead>
<tr>
<th>Algal species</th>
<th>Ea (kJ/mol)</th>
<th>A (s⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorella</td>
<td>29.82</td>
<td>0.1642</td>
<td>0.91</td>
</tr>
<tr>
<td>Spirulina</td>
<td>24.02</td>
<td>0.0699</td>
<td>0.83</td>
</tr>
</tbody>
</table>
Reaction Mechanisms

- First step, hydrolysis of proteins, carbohydrates and lipids
  - Proteins are hydrolyzed to produce amino acids
  - Carbohydrates are hydrolyzed to produce sugars
  - Lipids are hydrolyzed to produce fatty acids

- Second step, decomposition of amino acids, fatty acids and sugars
  - O is removed from carboxyl group to form carbon dioxide via decarboxylation
  - N is removed from amine group to form ammonia via deamination
  - Alkanes and alkenes are produced from fatty acids and organic acids via decarboxylation
  - Sugars are degraded to produce cyclic oxygenates

- Third step, recombination and decomposition of reaction intermediates
  - Carboxyl group in amino acid or fatty acid react with amine to produce N-heterocyclic compounds, such as pyrazine, pyrrole, etc.
  - Amino acid react with reducing sugar to produce N&O-heterocyclic compounds via Maillard reaction
  - Further recombination and decomposition of reaction intermediates
Summary and Conclusions

- Increase of temperature and retention time could increase the bio-crude oil yield and decrease the solid residue yield. For example, the yield of bio-crude oil produced from *Chlorella*, increased from 0.4% to 35.4% when the reaction temperature increased from 100°C to 300°C, and the solid residue yield decreased from 98.5% to 4.3%.

- Compared with uncatalyzed HTL, bio-crude oil could be increased about 10% by applying catalysts. Carbon deposition was found on the surface of metal catalysts after HTL.

- As reaction temperature and retention time increased, CR, NR and ER of bio-crude oil all increased. About 40% carbon and 75% nitrogen in the original algal feedstock remained in the aqueous phase.

- As temperature increased from 200°C to 300°C, fractions of hydrocarbons (3.3%-15.3%), amides (2.1%-14.8%), cyclic oxygenates (0.1%-5.1%) and heterocyclic compounds (4.7%-34.7%) in bio-crude oil increased. On the other hand, the fraction of organic acids decreased (58.9%-21.8%).

- The fraction of N & O heterocyclic compounds was largely increased with additions of alkaline catalysts(Uncatalyzed: 17.1%; NaOH: 26.1%; Na₂CO₃:36.1% ).

- A first-order decomposition kinetic model was derived. The activation energy for *Chlorella* and *Spirulina* decomposition was 29.8 kJ·mol⁻¹ and 24.0 kJ·mol⁻¹, respectively.
Demonstrated the feasibility to produce bio-crude oil from low-lipid microalgae via HTL.

Comprehensively investigated the effects of operating parameters, catalysts on product yields. Analysis of elemental distribution and energy balance provided justification for the design of E²-Energy.

Organic compounds in bio-crude oil were classified into groups to better elucidate the effects of operating parameters and catalysts.

A reaction pathway was proposed and a decomposition kinetic model was derived for HTL of low-lipid microalgae.
Recommendations & Future Work

- Upgrading of bio-crude oil
  - Decrease N & O content of oil samples

- Characterization of HTL products
  - Pretreatment of samples before GC-MS analysis

- Challenges for series HTL experimental design
  - The temperature ranges for protein, lipid and carbohydrates hydrolysis could overlap each other

- Kinetic study of HTL
  - Intrinsic kinetic model should be derived in the future
  - Eliminate effect of long heating time

- Life cycle assessment (LCA) of entire E²-Energy system
Acknowledgements

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• All of our BEE group members

• My Family
THANK YOU!