Hydrothermal Upgrading of Algae Paste: Application of $^{31}$P-NMR

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Outline

- Introduction
- Algal Biorefinery
- HTL and $^{31}$P-NMR technique
- Results
- Conclusion
Introduction

- Population rise from 6.6 billion today to 9.2 in 2050 = Increase in energy demand from 13 TW to 28 TW
- Rising CO₂ level: 280 ppm. (historic) to 390 ppm. today
- Fossil fuels not a long term option. Eventually it will run out !!!
- Options: Wind, Geothermal, Solar, Nuclear, Tidal, etc.
- Grow your own fuel: Biomass

*International Energy Association (2011), Technology Roadmap – Biofuels for Transportation*
Why Algae?

Sustainability:

- Social – Food vs. Fuel, Employment
- Environmental – Biodiversity, Water/Land use, Carbon Emission
- Economic – Investment, Finance and Cost !!!

**Oil Yield (L/ha/yr)**

- Corn: 172
- Soybean: 446
- Peanut: 1059
- Rapeseed: 1190
- Palm: 5950
- Algae: 95000

*Gao et al. (2012), Chemistry Central Journal, DOI: 10.1186/1752-153X-6-S1-S1*
Microalgae Biorefinery

An integrated process to synthesise biofuels, biochemicals and by-products from sustainable feedstock

- Utilise every aspect of biomass to make something useful
- Each process tailor made for use with algae to produce required product

3 Process routes:
- (Wet) Route 1 – Gasification/Liquefaction
- (Dry) Route 2 – Conventional method of extraction and separation
- (Dry) Route 3 - Pyrolysis

Patel et al. (2012), ISRN Renewable Energy, DOI: 10.5402/2012/631574
**Wet Processing Route (Liquid Product)**

- Energy saving of approx. 50% by circumventing drying
- Potential to use algae cultivated in wastewater
- Nutrient recycling
- Bio-crude yield greater than lipid content
- Direct production of biodiesel possible with addition of ethanol/methanol
- Exploit properties of hydrothermal water

### Process Step

<table>
<thead>
<tr>
<th>Process Step</th>
<th>Dry Algae Biomass (MJ/kg)</th>
<th>Wet Algae Biodiesel (MJ/kg)</th>
<th>HTL for Biocrude (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Culture and Harvesting</td>
<td>7.5</td>
<td>10.6</td>
<td>10.6</td>
</tr>
<tr>
<td>Drying</td>
<td>90.3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Extraction</td>
<td>8.6</td>
<td>30.8</td>
<td>28-54*</td>
</tr>
<tr>
<td>Oil Tranesterification</td>
<td>0.9</td>
<td>0.9</td>
<td>38.6 - 64.6</td>
</tr>
<tr>
<td>Total</td>
<td>107.3</td>
<td>42.3</td>
<td>38.6 - 64.6</td>
</tr>
</tbody>
</table>

Adapted from Lardon et al. (2009), Environmental Science and Technology, DOI: 10.1021/es900705j
Biller et al. (2011), Bioresource Technology, DOI: 10.1016/j.biortech.2010.06.028

*HTL liquefaction: Calculated on basis of Energy Recovery and Energy Consumption Ratio
**Experimental Methodology**

**Organic Phase and Solids Analysis**

- **GC-MS**
- **ICP**
- **Ion Exchange Chromatography**

**Aqueous Phase (Sample)**

- **Gas Syringe Analysis**
  - GC

**Gas Phase**

- **Analysis**
  - TOC
  - GC-MS
  - ICP
  - Ion Exchange Chromatography

**Dry Solid Residue Analysis**

- **1H NMR**
- **13C NMR**
- **31P NMR**

**Biochar**

- **Analysis**
  - HCN

**Recovered Aqueous Phase (325°C)**

- **T=5, 10, 15, 30, 60**
HTU – Overall Yield of Oil, Solid and Gas

• Investigated Parameters:
  • Temperature (275-380°C)
  • Residence Time (5-60 min)
  • Algal to water ratio of 1:3.5 (wt.-%)

• Highest yield (38 wt.-%) at 5 min and 380°C. HHV: 43 MJ/kg

• For Oil Yield:
  • Effect of Temperature > Residence Time

• For Biochar Yield:
  • Effect of Residence Time > Temperature

• Gas predominantly composed of CO₂.

• N known to partition into solids and aqueous phase. N balance between three phases needs to be investigated
**31P – NMR for Oil Analysis (Deoxygenation)**

- Analysis of bio-crude using conventional techniques is time consuming and sometimes not so informative, especially if quantitative data is required.

- OH group can be derivitised using a Phosphylation agent TMDP (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane) and analysed using $^{31}$P-NMR for extent of deoxygenation.

- Rapid quantitative analysis can be carried to obtain deoxygenation reaction kinetics based on transformation in function group.
TMDP derived sample quantified using Internal Standard HNDI (N-hydroxy-5-norbornene-2,3-dicarboximide)

Acidic, Aliphatic, Aromatic, Guacyl, and Phenolic OH shifts identified

Excess TMDP used to ensure complete derivation

Acidic region from lipids (phospholipids, galactolipids and triglyceride)

Rapid OH removal in the first 5 minutes followed by gradual decrease

Possibility of occurrence of Fischer-Tropsch type reaction (all reactants present)

* $t_0$ found by OH content of lipids
$^{31}$P – NMR: Aliphatic, Aromatic and Phenolic OH

- Largest contributor of observed deoxygenation is from Aliphatics
- Possible link between Carbohydrate degradation and protein hydrolysis. Interaction leads to formation of intermediates (Aromatics and Condensed Phenolic)

* $t_0$ found by polysaccharide hydrolysis in Ionic Liquid
Carbohydrate and Protein decomposition is governed by a complex set of reactions which produce interesting intermediates.

Model compound study on Carbohydrates and Protein interaction is of great importance for algae liquefaction.
Deoxygenation: Elemental vs. $^{31}$P-NMR

- Overall reduction in OH is observed in both elemental and $^{31}$P-NMR.

- Substantial difference between the two. Implying presence of multiple deoxygenation mechanisms.

- Limitation of $^{31}$P-NMR: Esters, Ethers, and Ketones do not react with TMDP, thus they are not detected.

- Elemental analysis fails to provide information on molecular group transformation. $^{31}$P-NMR provides information at molecular level.

* $t_0$ found by addition of Organic and Aliphatic OH
Simulated Distillation and GC-MS

- Sample from 275 and 380°C and 30 minute residence time
- Produced biocrude significantly different from fossil crude
- HTL alone is not sufficient to make usable biocrude
- Lighter components prevalent in biocrude from higher temperature. But do not seem to improve biocrude property
Conclusion

• HTL of algae paste was carried out at various temperature and residence time. TMDP reactive moieties were analysed using $^{31}$P-NMR

• Similar oil yield within 10 minutes at all temperatures but biochar and gas produced inversely related

• Aliphatic and Lipid OH show most significant reduction. Protein + Carbohydrate interaction results in intermediates formation. Warrants further investigation.

• Significant deoxygenation observed at short residence time (<10 mins). Increasing residence time does not remove substantial oxygen, but redistributes/reorganises compound

• $^{31}$P-NMR is a useful platform to measure changes in hydroxy moiety and identify transformations taking place in a complex reaction
Future Work - Flow Reactor

- Flexibility over pressure (<220 bar), temperature (<400°C) and residence time (1 sec – 10 mins). Better control over reaction parameters.

- Also used for in situ transesterification of algae paste and biocrude production

- Trial runs in progress
Thank you for listening

Prospect of SCW

Use water at high temperature (200-400°C) to break macromolecules

- Lower dielectric constant and better Hildebrand solubility parameter

- Enhancement of Acid/Base catalysed reactions. $K_w (K_w = [\text{OH}^-]_{aq} [\text{H}^+]_{aq})$ increases threefold from $10^{-13.99}$ to $10^{-11.30}$ at 25 to 300°C respectively

- Nitrogen recovery in aqueous phase

- Converts energy content of dry algae to yield higher energy content product

- Greater deoxygenation compared to pyrolysis: energy content, thermal stability and corrosive

*Peterson et al. (2012), Energy & Environmental Science, DOI: 10.1039/b810100k*