

# Conversion of Wet Algal Biomass Into Liquid Fuels Through Hydrothermal Liquefaction: Review and Recent Developments

10/27/11

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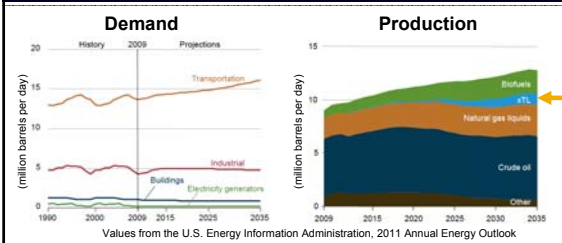
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## Problem: Increased Demand of Liquid Fuels in the US

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- Projected demand for Biofuels and Biomass-to-Liquid fuels

- 3 million barrels per day by 2035 (~20%)



Energy Information Administration 2011.

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## What's the pathway?

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Biomass  $\xrightarrow{?}$  Fuel



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## Proposed Feedstock: Microalgae

### Microalga Feedstock

- High production yields (10× oilseed crops)
- High lipid/protein content
- Ability to capture carbon emissions
- Ability to treat waste water
- Small cell size, ~1-10µm (no need for milling)



Nanochloropsis sp. slurry

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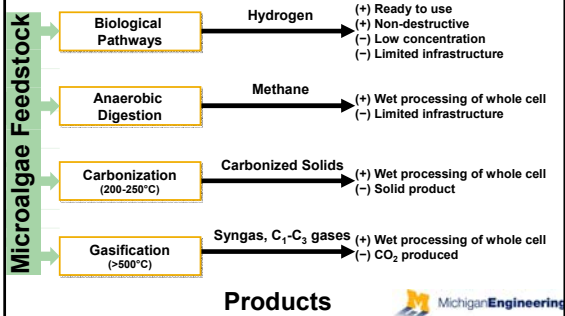
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## Microalgae-to-Fuels Pathways




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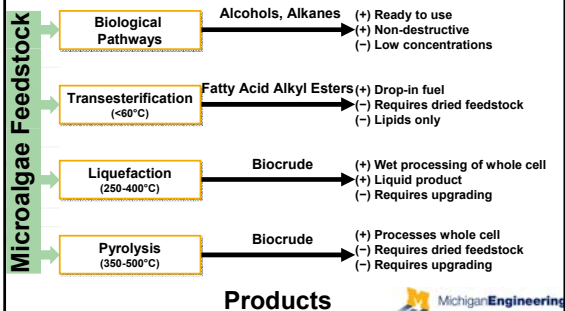
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## Microalgae-to-Liquid Fuels Pathways




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## Proposed Conversion Technique: Hydrothermal Liquefaction

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- Converts wet biomass (Some dewatering)
  - High Temperature Water (250-400°C)
  - High Pressure ( $\geq$ Sat. Pressure of H<sub>2</sub>O)
- Produces energy dense biocrude



Biocrude from the liquefaction of *Nannochloropsis* sp.

Y. Dote et al. 1994, P. Biller & A. Ross 2011, Y. Yang et al. 2004, T. Mironov et al. 1995, T. Brown et al. 2010.




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## Proposed Conversion Technique: Hydrothermal Liquefaction

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- Converts wet biomass (Some dewatering)
  - High Temperature Water (250-400°C)
  - High Pressure ( $\geq$ Sat. Pressure of H<sub>2</sub>O)
- Produces energy dense biocrude
- Produces other valuable co-products
  - Reuse in the feedstock cultivation or biocrude production
  - Use in other industries

Y. Dote et al. 1994, P. Biller & A. Ross 2011, Y. Yang et al. 2004, T. Mironov et al. 1995, T. Brown et al. 2010.




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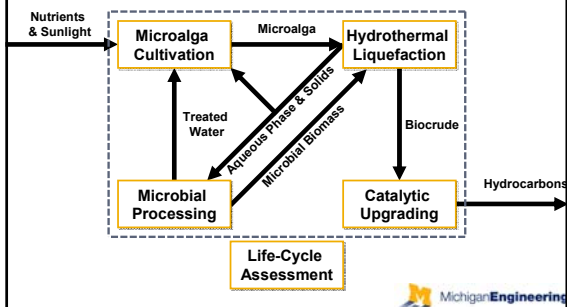
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## Hydrocarbons from Biomass Project (HyBI)

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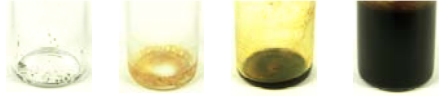
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## Liquefaction Products

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Gas	Solids (solvent insoluble)	Water-soluble Products	Light Biocrude (hexane soluble)	Heavy Biocrude (dichloromethane soluble)
H <sub>2</sub> , CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , CO	ash, salt, some organic	short-chain carboxylic acids, amino acids, glycerol, phosphate	branched alkanes, aromatics, oxygenated/nitrated hydrocarbons, long-chain fatty acids	organic compounds >300amu
 <p>Solvent-free products</p>				

T. Brown et al. 2010, Valdez et al. 2011. Michigan Engineering

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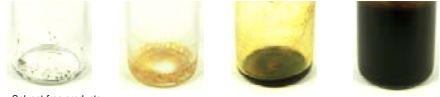
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## Desired Product Characteristics

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Gas	Solids (solvent insoluble)	Water-soluble Products	Light Biocrude (hexane soluble)	Heavy Biocrude (dichloromethane soluble)
Low yield Low CO <sub>2</sub> yield	Just ash and minerals No organic	Recovery of remaining C, H, N, S, O N recovered as NH <sub>3</sub>	High yield High C, H content Low O, N, S content	Low yield High C, H content Low O, N, S content
 <p>Solvent-free products</p>				

Michigan Engineering

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## Research Goals

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- Examine how processing conditions affect product yields and characteristics
- Identify parameters that result in desired product characteristics
- Build foundation for methodology to predict product yields and composition

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## Research Methodology

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- Vary time and temperature
- Measure:
  - Yield (mass product / mass microalga)
  - Elemental content (mass element / mass product)
  - Elemental recovery (mass element / mass of element in microalga)
  - Energy recovery (energy in product / energy in microalga)




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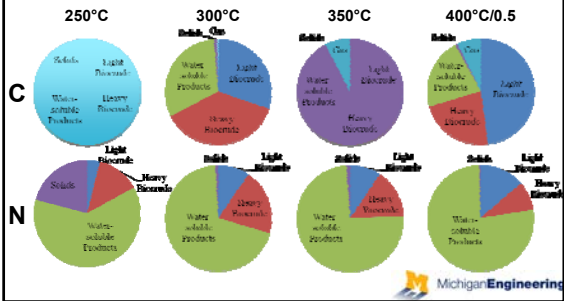
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## Elemental Recovery

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- 20 min.  
250°C




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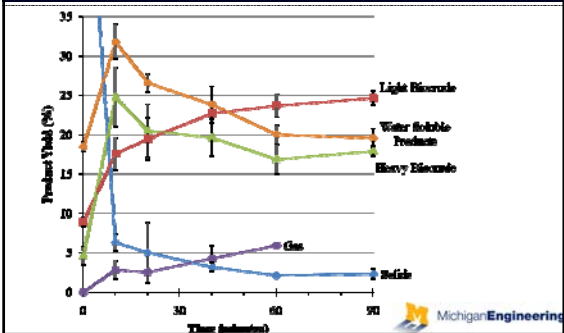
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## Liquefaction Products at 350°C

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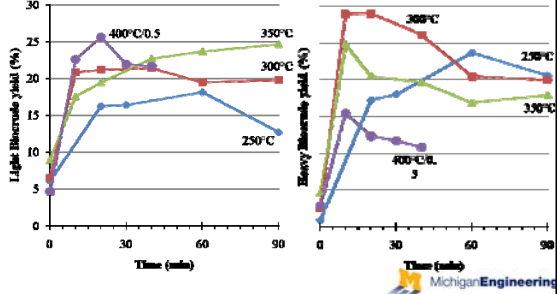
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## Biocrude Yield

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■ Combined Biocrude Yields of 40 - 50%




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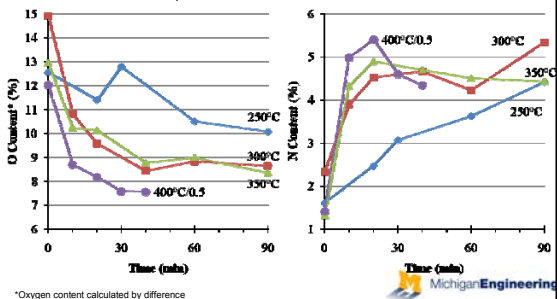
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## C, N, O, S in the Light Biocrude

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■ C: 73 – 77%, S: 0.4 – 0.6%



\*Oxygen content calculated by difference

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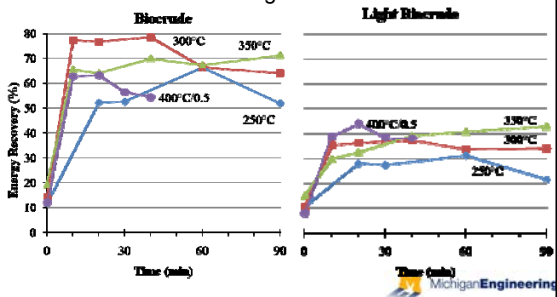
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## Biocrude: Energy Recovery

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■ Estimated from Dulong's formula for HHV




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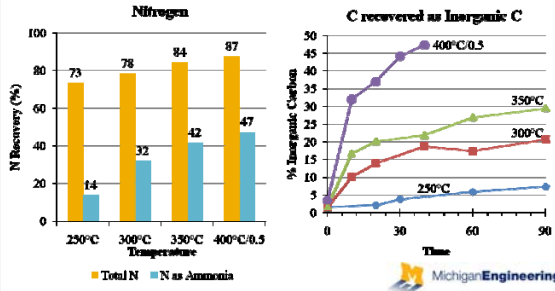
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## Water-soluble products: C & N Recovery

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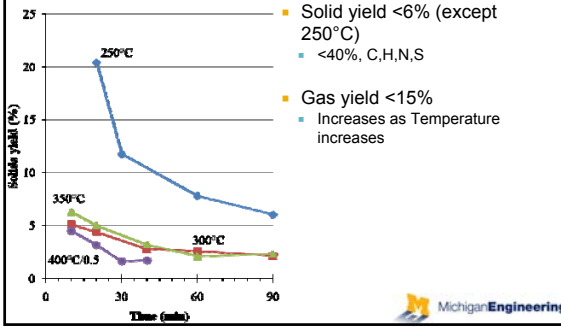
- 25-45% of the carbon is recovered



## Gas and Solids

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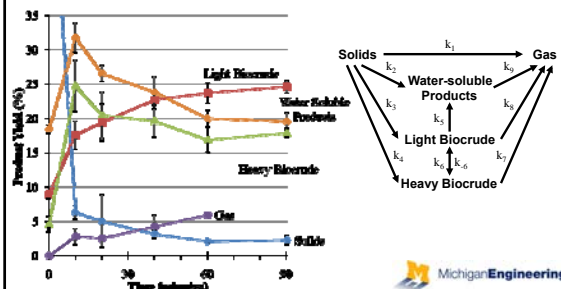
- Solid yield <6% (except 250°C)
- <40%, C,H,N,S
- Gas yield <15%
- Increases as Temperature increases



## Proposed Reaction Network

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- Based on evidence from time/temperature data



## Conclusions

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- Some desired characteristics achievable with simple parameter variation
  - Product yields are temperature and time dependent
  - >50% of the energy in the alga is recovered in the biocrude, >40% energy recovery in the Light Biocrude at 350, 400°C
  - Conditions for reducing O content in the Light Biocrude also results in an increased N content
- >70% of the N is recovered almost immediately in the Aqueous phase
- Progress towards an in-depth kinetic analysis



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## Future Work

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- Investigate shorter residence times
- Confirm proposed reaction network
- Derive kinetic model
  - Working model for estimating yield and elemental composition,  $f(x_i, t, T)$ ,  $f(x_{C,i}, t, T)$

$$\frac{dx_i}{dt} = k_i f(x_i) \quad k_i(T) = A_i e^{-\frac{E_{a,i}}{RT}}$$

$$\frac{dx_{WSP}}{dt} = k_2 f(x_S) + k_5 f(x_{LB}) - k_9 f(x_{WSP})$$

$$\frac{dx_{C,WSP}}{dt} = k_{C,2} f(x_{C,S}) + k_{C,5} f(x_{C,LB}) - k_{C,9} f(x_{C,WSP})$$



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## Acknowledgements

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- Mike Nelson
- Nick Garza
- Savage Research Group



Grant EFRI-0937992



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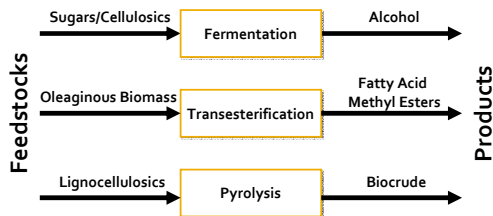
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## Common Biomass-to-Liquid Fuels Pathways

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## Conversion Techniques

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Process	Product	Temperature Range (°C)	Advantages	Disadvantages
Natural Products	Alkanes, Alcohol, Hydrogen	N/A	Minor post-processing	Low concentrations, Specific/Modified Species
Transesterification	Fatty Acid Methyl Esters	<60	Drop-in Fuel	Dried, Lipids Only
Anaerobic Digestion	Biogas	N/A	Whole Cell	Gas Product
Pyrolysis	Biocrude, Gases	350-500	Whole Cell	Dried
Torrefaction	Biocrude	250-350	Whole Cell	Dried
Carbonization	Carbonized Solids	200-250	Whole Cell	Dilute, Solid Product
Gasification	Gases	>500	Whole Cell	Dilute, Gas Product
Hydrothermal Liquefaction	Biocrude	250-400	Whole Cell, Liquid Product	Dilute




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## Motivation

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### Summary of alga liquefaction studies

Reference	Microalgal Feedstock	Parameters Studied
Dote et al.	<i>Botryococcus braunii</i>	Temperature, Catalyst
Yang et al.	<i>Microcystis viridis</i>	Temperature, Time (2), Catalyst
Minowa et al.	<i>Dunaliella tertiolecta</i>	Temperature, Time (2), Catalyst
Brown et al.	<i>Nannochloropsis</i> sp.	Temperature
Valdez et al.	<i>Nannochloropsis</i> sp.	Recovery Solvent
Duan & Savage	<i>Nannochloropsis</i> sp.	Catalyst, Headspace Composition
Billar & Ross	<i>Chlorella vulgaris</i> , <i>Nannochloropsis oculata</i> , <i>Porphyridium cruentum</i> , <i>Spirulina</i> sp.	Catalyst, Feedstock
Ross et al.	<i>Chlorella vulgaris</i> , <i>Spirulina</i> sp.	Temperature, Catalyst, Feedstock
Jena et al.	<i>Spirulina platensis</i>	Temperature, Time <sup>b</sup> , Loading

<sup>a</sup>Yield calculated as mass biocrude per mass dry and ash free biomass  
<sup>b</sup>Examined 5 timepoints but for a single temperature




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## Motivation

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Reference	Microalgal Feedstock	Biocrude Yield (%)	Parameters Studied
Yang et al.	<i>Microcystis viridis</i>	33 <sup>a</sup>	Temperature, Time (2), Catalyst
Minowa et al.	<i>Dunaliella tertiolecta</i>	31-44 <sup>a</sup>	Temperature, Time (2), Catalyst
Jena et al.	<i>Spirulina platensis</i>	~30-60	Temperature, Time <sup>b</sup> , Loading

### What's Missing?

- Groundwork for reaction engineering of liquefaction of microalga
  - Systematic study of time dependence
  - Design of a reaction network
  - Determination of reaction rates and Arrhenius parameters

<sup>a</sup>Yield calculated as mass biocrude per mass dry and ash free biomass  
<sup>b</sup>Examined 5 timepoints but for a single temperature




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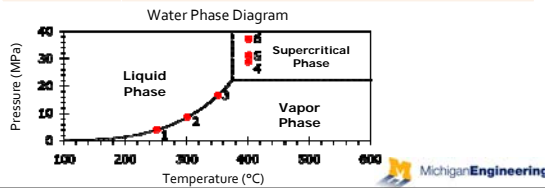
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## Experimental Design

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### Variables:

Parameter	1	2	3	4	5	6
Temperature (°C)	250	300	350	400	400	400
Pressure (MPa)	4.0	8.6	16.5	28.8	31.2	37.2
Water Density (g/mL)	0.799	0.712	0.575	0.5	0.4	0.3
Time (min)	10-90					




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## Experimental Design

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### Variables:

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Water Density (g/mL)	0.799	0.712	0.575	0.5	0.4	0.3
Time (min)	10-90					

### Fixed Parameters:

- *Nannochloropsis* sp.
  - C: 51%, H: 7%, N: 9%, S: 0.6%, O: 29.4%, ash: 3%
  - 59% proteins, 14% lipids, 20% carbohydrates
- 15 wt % alga solids concentration in water




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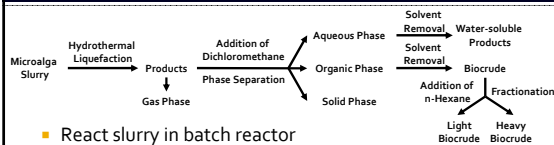
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## Experimental Procedure

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- React slurry in batch reactor
  - Fast heat-up (<3 min.)
- Collect products for analysis



4mL Swagelok® reactor with gas sampling valve




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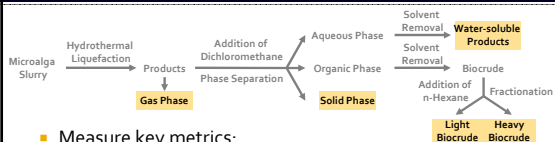
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## Experimental Procedure

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- Measure key metrics:
  - Yield (mass product / mass microalga)
  - Elemental content (mass element / mass product)
  - Elemental recovery (mass element / mass of element in microalga)

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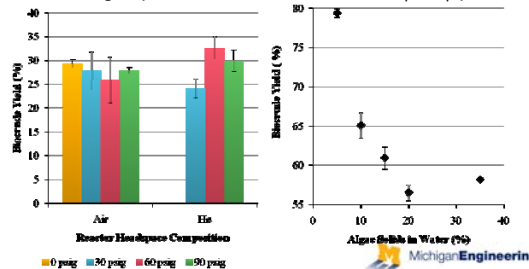
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## Results

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- Atmosphere Effects
  - Nannochloropsis, 350°C
- Loading Effects
  - Nannochloropsis sp., 350°C




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## Reactor Types

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	Autoclave	Swagelok®
References	Dote, Duan, Yang, Minowa, Zhou, Ross (unstirred)	Brown, Duan
Size	>75mL Volume	<31mL Volume
Advantages	Stirred Temperature & Pressure Monitoring	Fast Heat up (>100°C/min.) Less Solvent for work-up
Disadvantages	Slow Heat-up (<25°C/min.)	



Figure 1. Fundamental options for reactors. Y. Dote, S. Sawagama, S. Inoue, T. Minowa, S.-Y. Yokoyama, Recovery of liquid fuel from hydrocarbon-rich microalgae by hydrothermal liquefaction, (1994) 1855-1857

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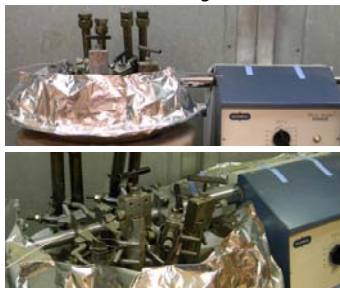
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## James Bond Reactor

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- Shaken (not stirred) gas valve reactors



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## FTIR Spectroscopy

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- Measures infrared radiation absorbed by a compound
- Absorption wavenumbers correspond to specific molecular bonds

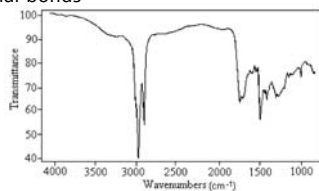


Figure 7. FT-IR spectrum of crude bio-oil (PAC, no H<sub>2</sub>).

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## NMR Spectroscopy

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- In a magnetic field, nuclei are excited from  $\alpha$  to  $\beta$  spin states using radio frequency radiation
  - At a resonance frequency, a response can be measured

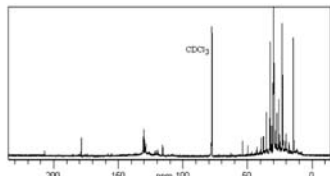


Figure 6. <sup>13</sup>C NMR of bio-oil in CDCl<sub>3</sub> (PAC, no H<sub>2</sub>).

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