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

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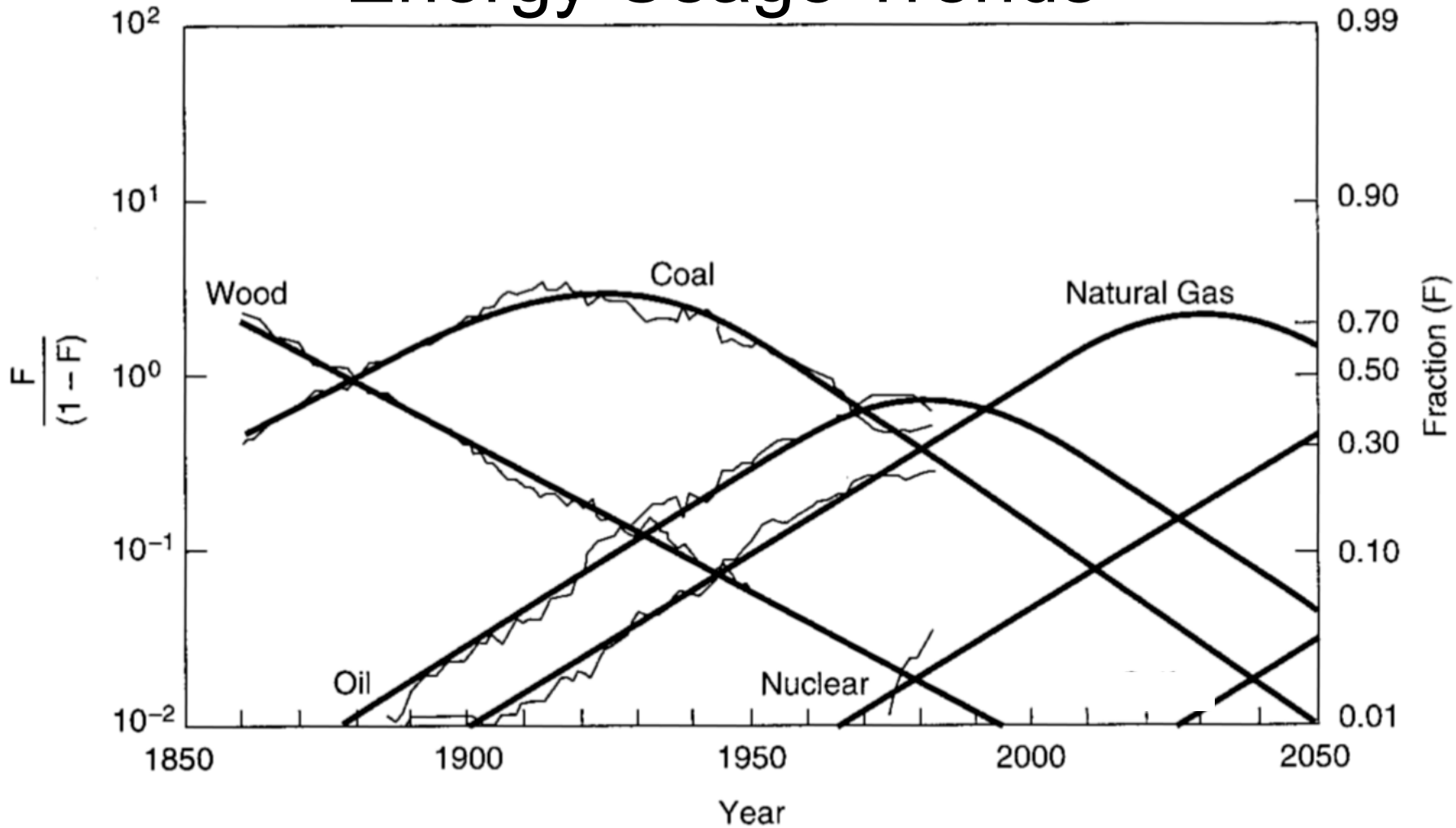
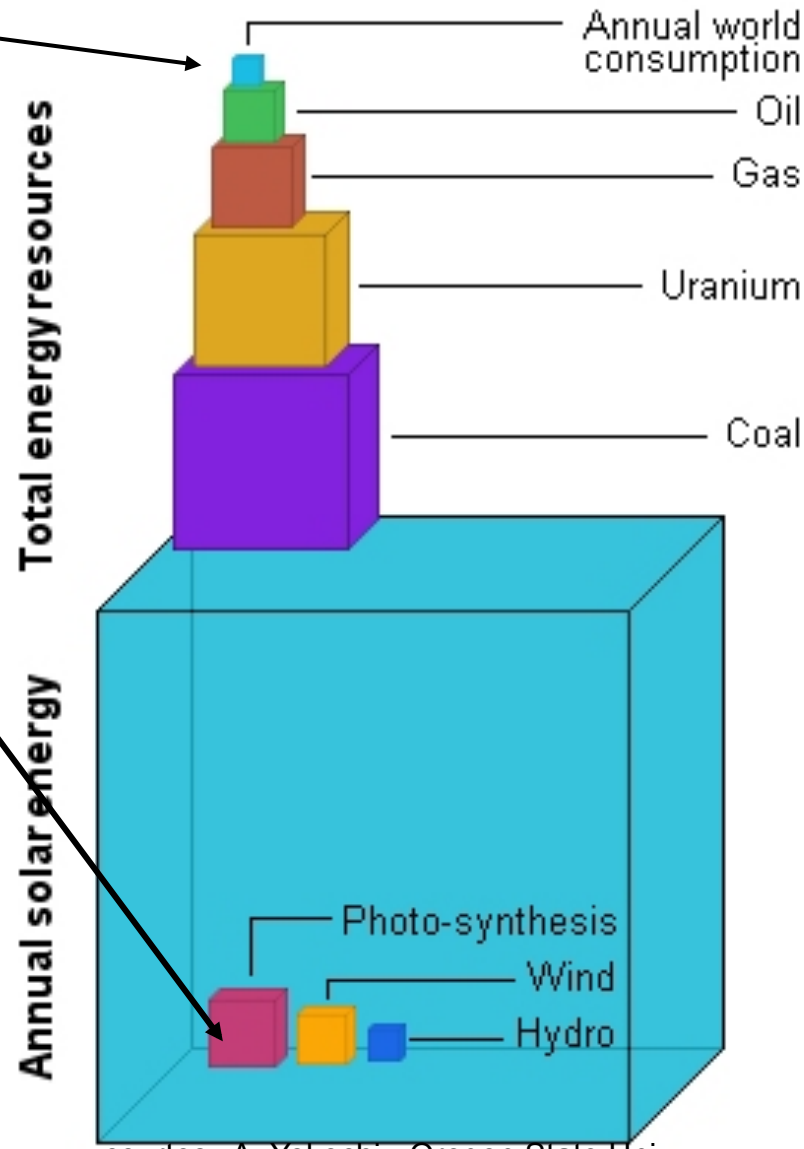
Energy Usage Trends



society transitions to new energy sources when it improves life - not because of scarcity

Why Liquid Fuels from Biomass?

~ 15 TW
~ 450 quads



courtesy A. Yokochi - Oregon State Univ

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.

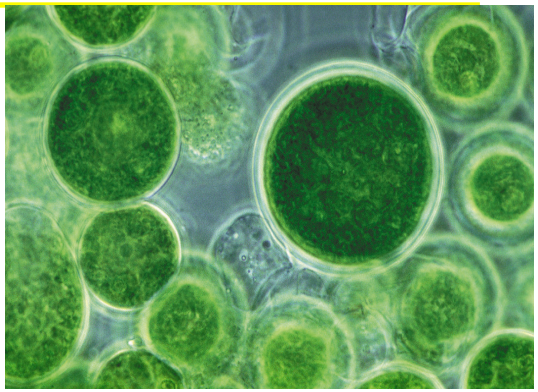
Can algae be a better biofuel feedstock?

- 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

Crop	Oil Yield (L ha^{-1} y^{-1})
Soybean	450
Camelina	560
Sunflower	955
Rapeseed	1,190
Jatropha	1,890
Oil Palm	5,950
Microalgae	**3,800-50,800**

Chisti Y. Biodiesel from microalgae. Biotechnol Adv 2007;25(3):294-306.

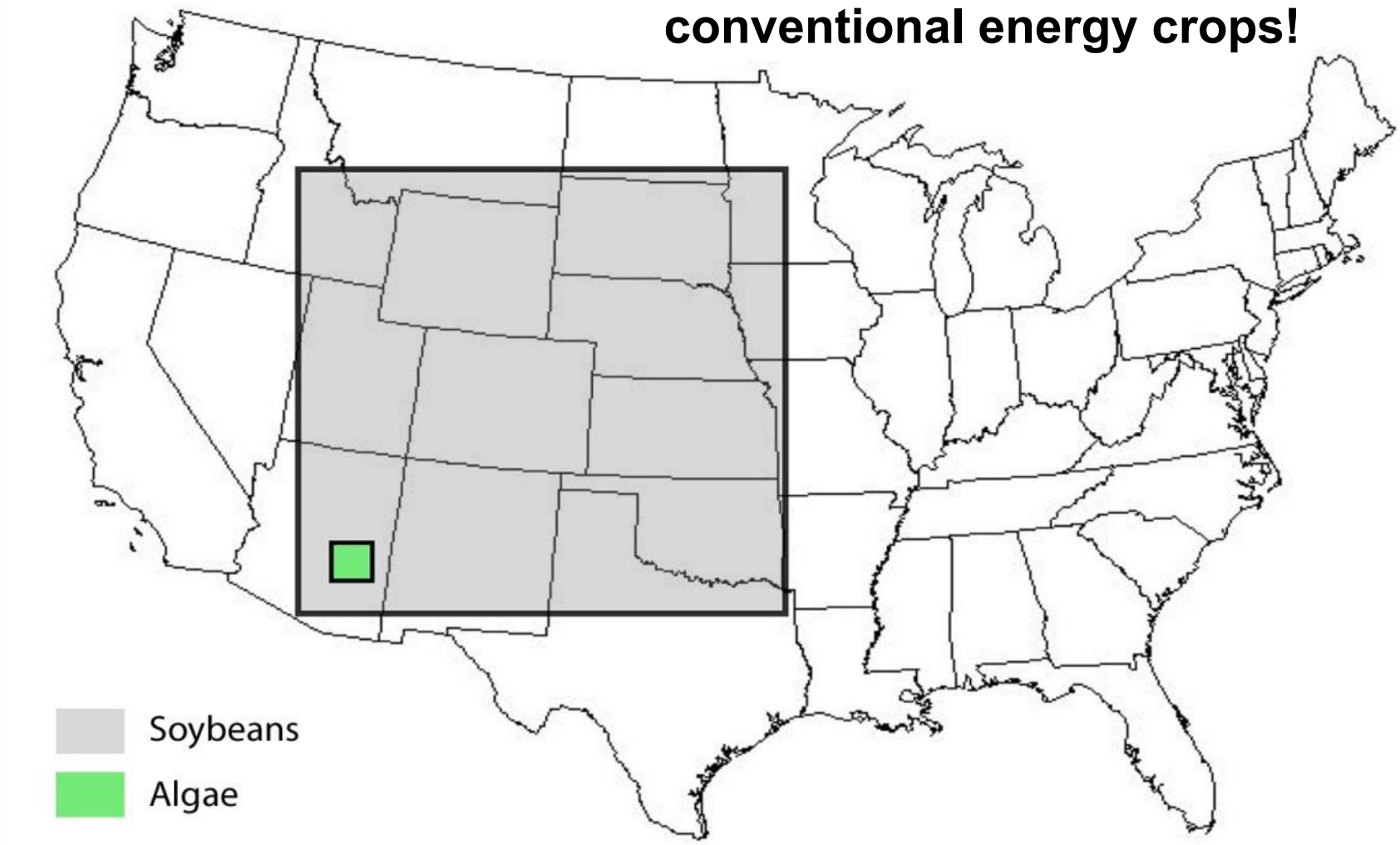
Microalgae



- 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

Land Area to Replace 50% of Petroleum Distillates

Algae need much less land than conventional energy crops!



Adapted from Bryan, et al. (2008)

Going REALLY green: World's first bio-building powered by ALGAE opens in Hamburg

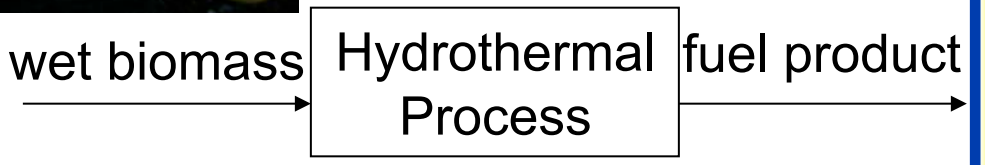
Biofuel from Microalgae

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

- $$$$, 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_2O at 200 – 350°C (T_C = 374°C)

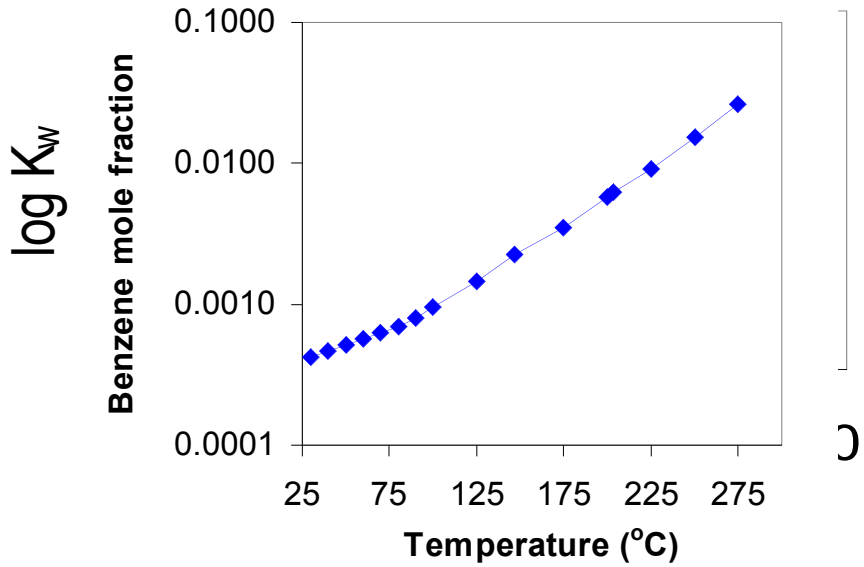
Properties of HTW different from room-temperature water

- Fewer and less persistent H-bonds
- Lower dielectric constant

  → Increased solubility of organic compounds

- Higher $K_W = (H^+)(OH^-)$

  → enhanced acid catalysis



Hydrothermal Routes from Wet Algae to Biofuels

Wet Biomass (algae)

Carbonization ~ 200 °C → Fatty Solids

Fatty Solids → *Esterification (Solvothermal)* → Crude Biodiesel

US Patent: 2012/0079760A1

Fatty Solids → *Deoxygenation* → Hydrocarbon Fuel

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

Crude Bio-oil → *Upgrade* → Hydrocarbon Fuel or Oil

US Patent: 2012/0055077A1

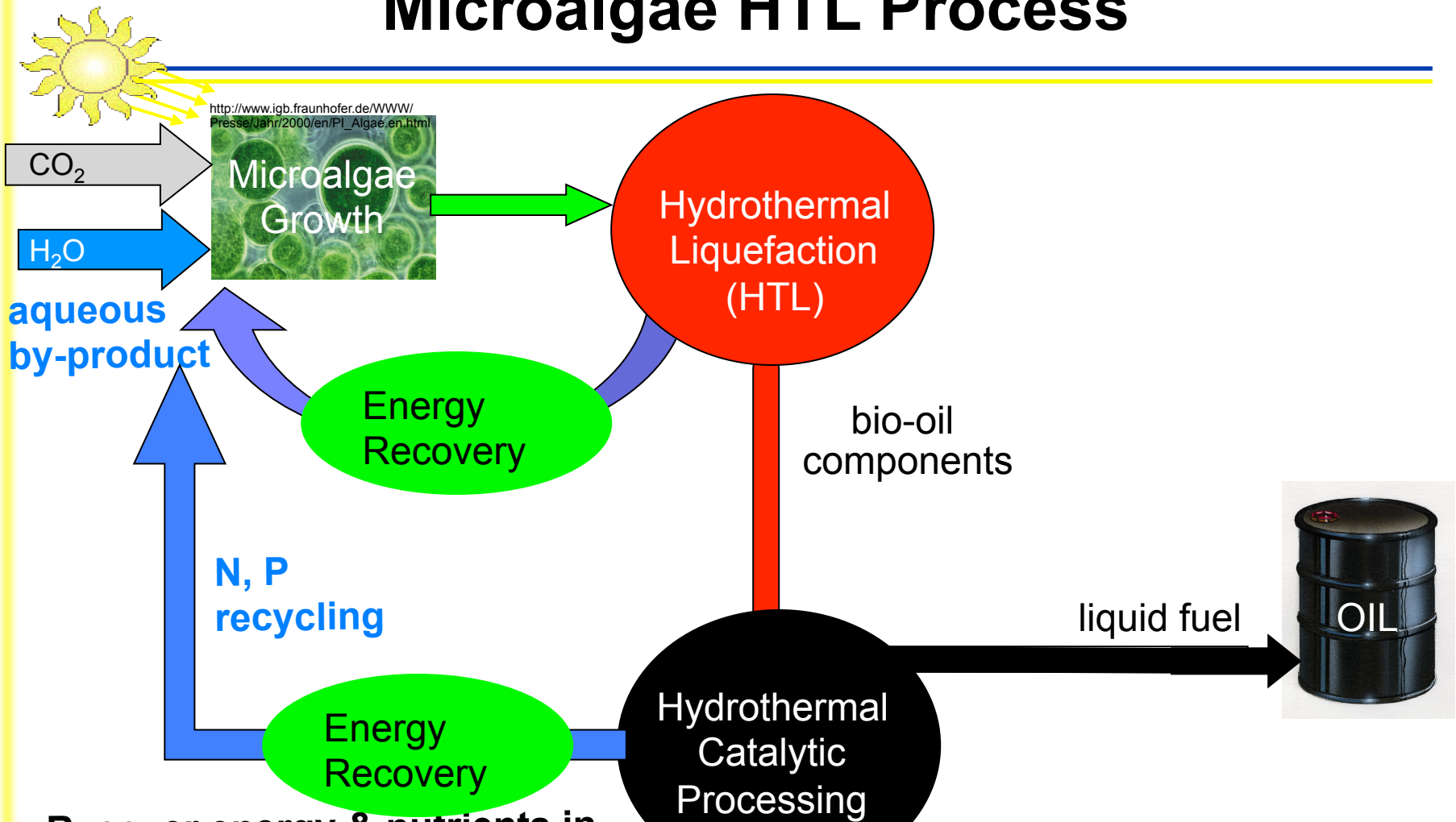
Wet Biomass (algae) → *Gasification* ~ 600 °C → CH_4, H_2

CH_4, H_2 → Hydrocarbon Fuel or Oil

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



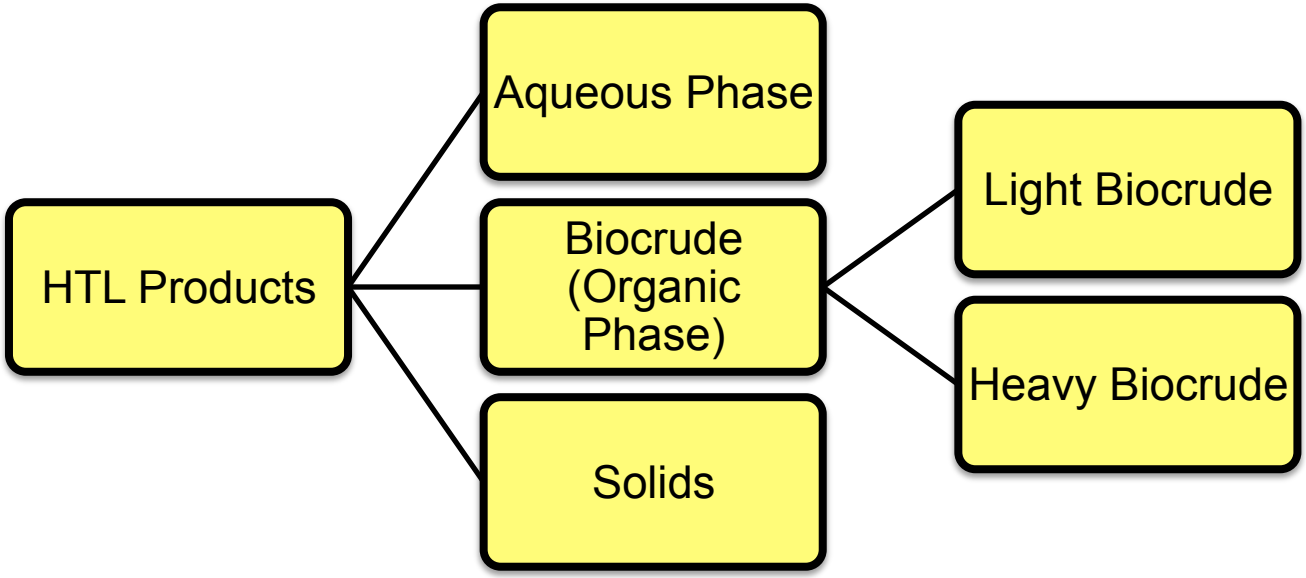
Recover energy & nutrients in aqueous stream – essential for energy-positive & sustainable process

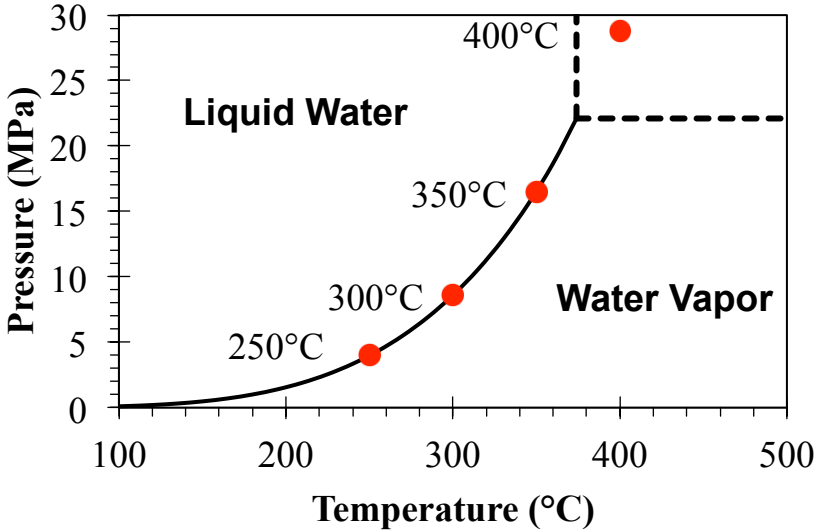
Hydrothermal Liquefaction of Microalgae

wet algal biomass → Hydrothermal Liquefaction → Crude bio-oil

Brown, Duan, Savage, *Energy & Fuels*, 2010
Valdez, Dickinson, Savage, *Energy & Fuels*, 2011
Duan, Savage, *Ind. Eng. Chem. Res.*, 2011
Valdez et al., *Biomass & Bioenergy*, 2012
Valdez & Savage, *Algal Research*, 2013

Experimental Procedure





Elemental Analysis of Bio-Crude

Temp. (°C)	C	H	O	N	S
Dry Algae	43.3	6.0	25.1	6.4	0.53
200	74.6	10.8	11.8	2.4	0.44
300	75.2	10.3	9.8	4.3	0.79
400	76.7	10.3	8.7	3.6	0.91
Crude Oil[2]	83-87	10-14	0.1-1.5	0.1-2.0	0.5-6.0

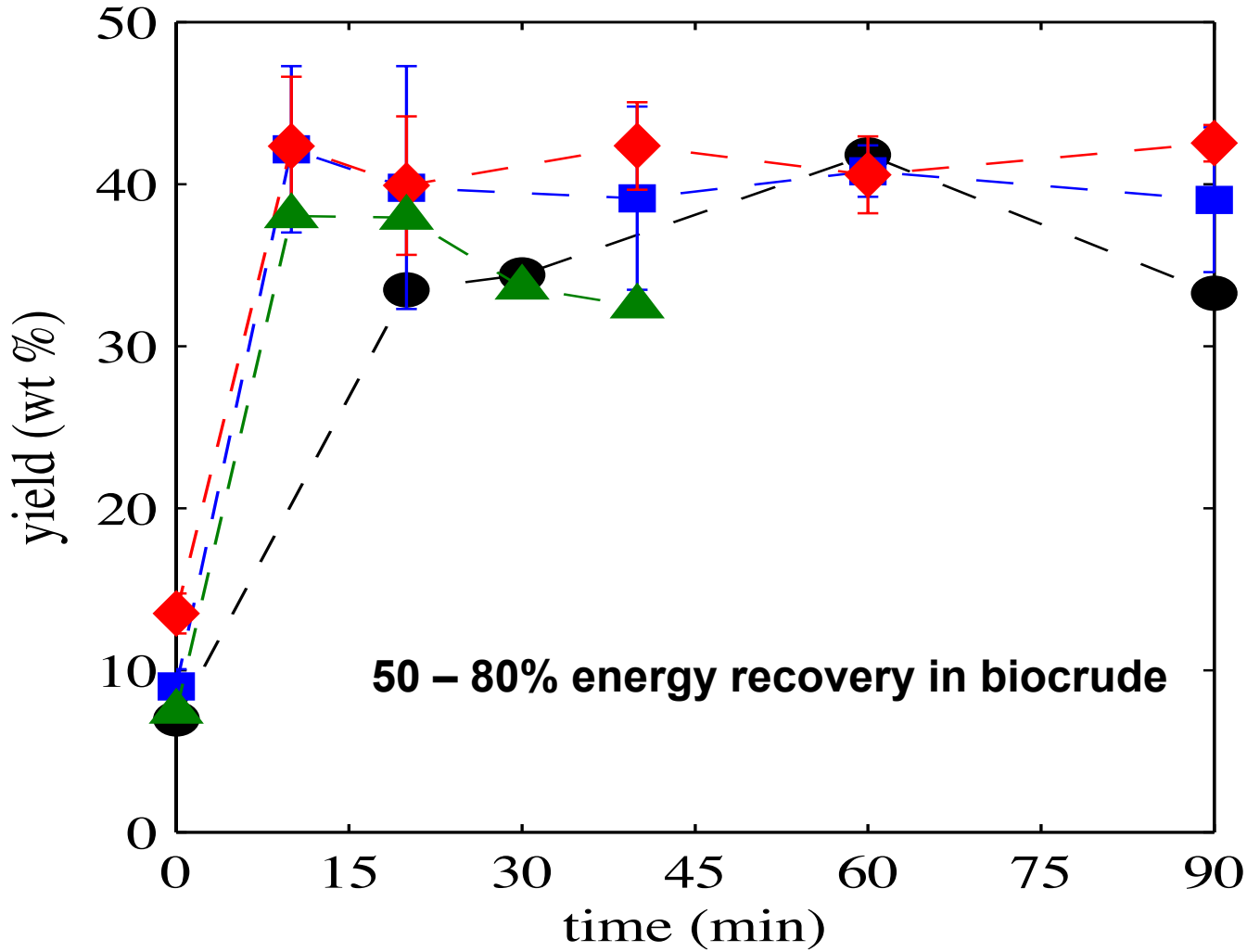
From Brown, Duan, & Savage., *Energy & Fuels.* 2010

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

Nannochloropsis sp.

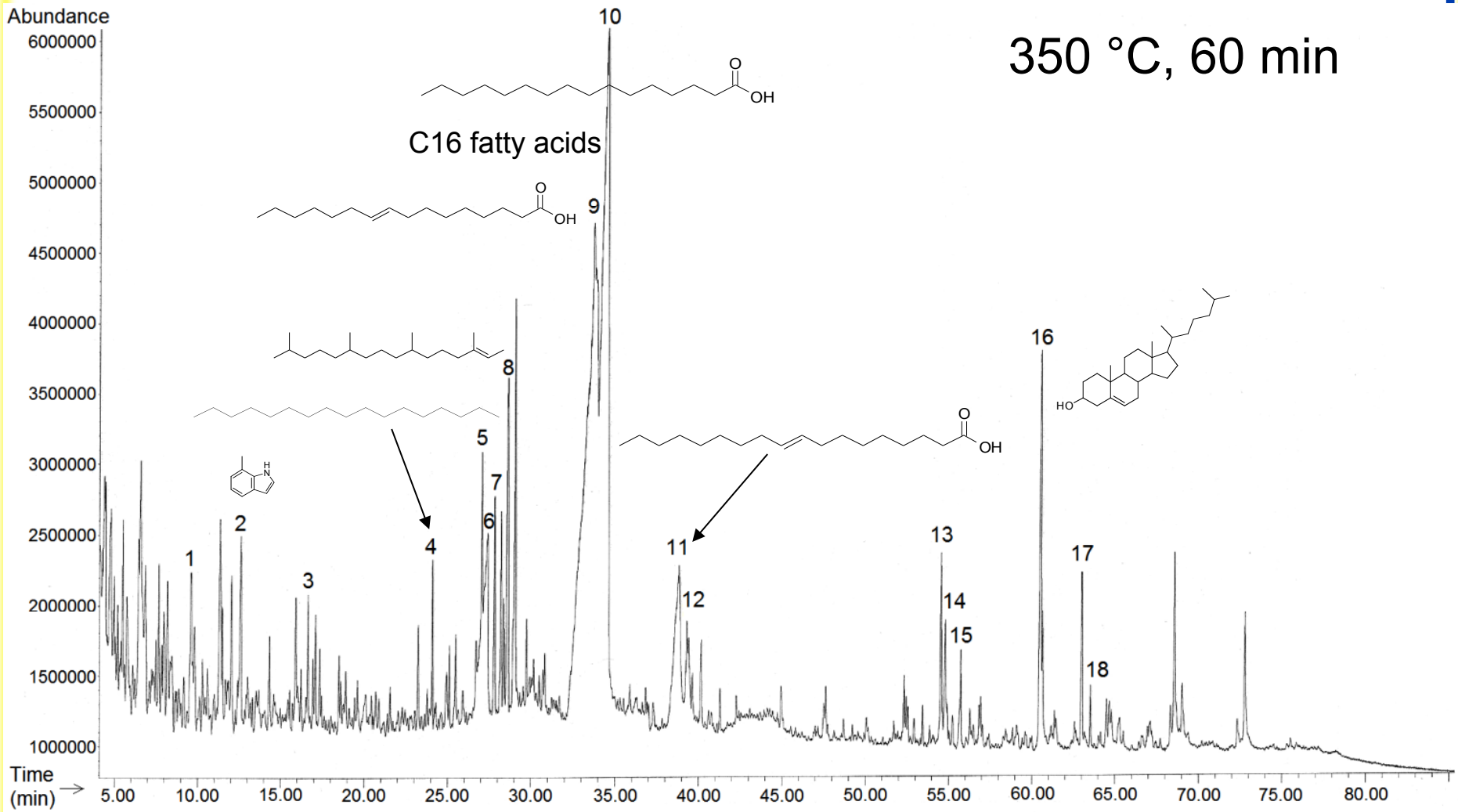
[2]**Data from http://en.citizendium.org/wiki/Petroleum**

Biocrude Yields (wt%) from Isothermal HTL

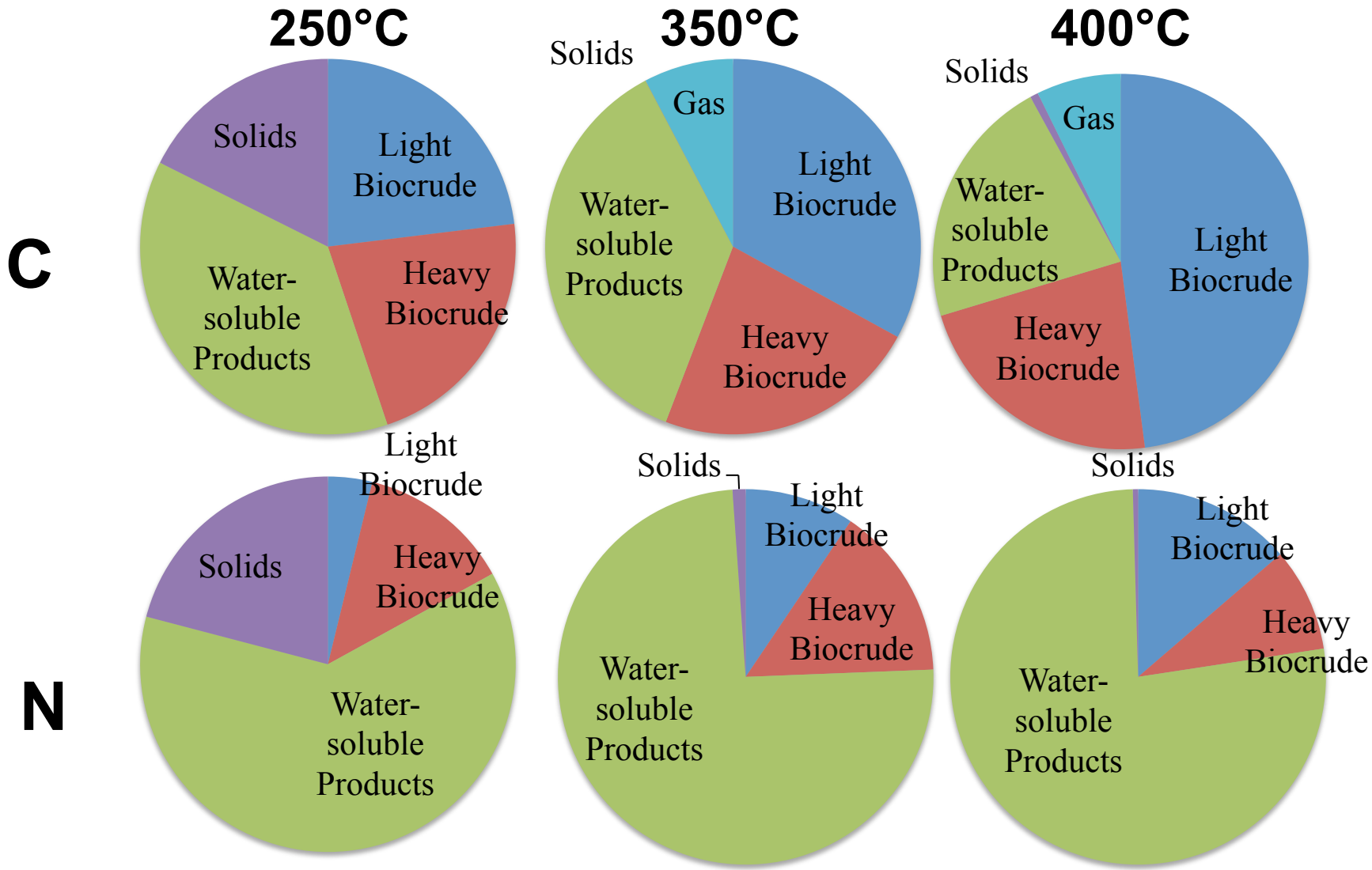


Valdez et al., *Biomass & Bioenergy*, 2012

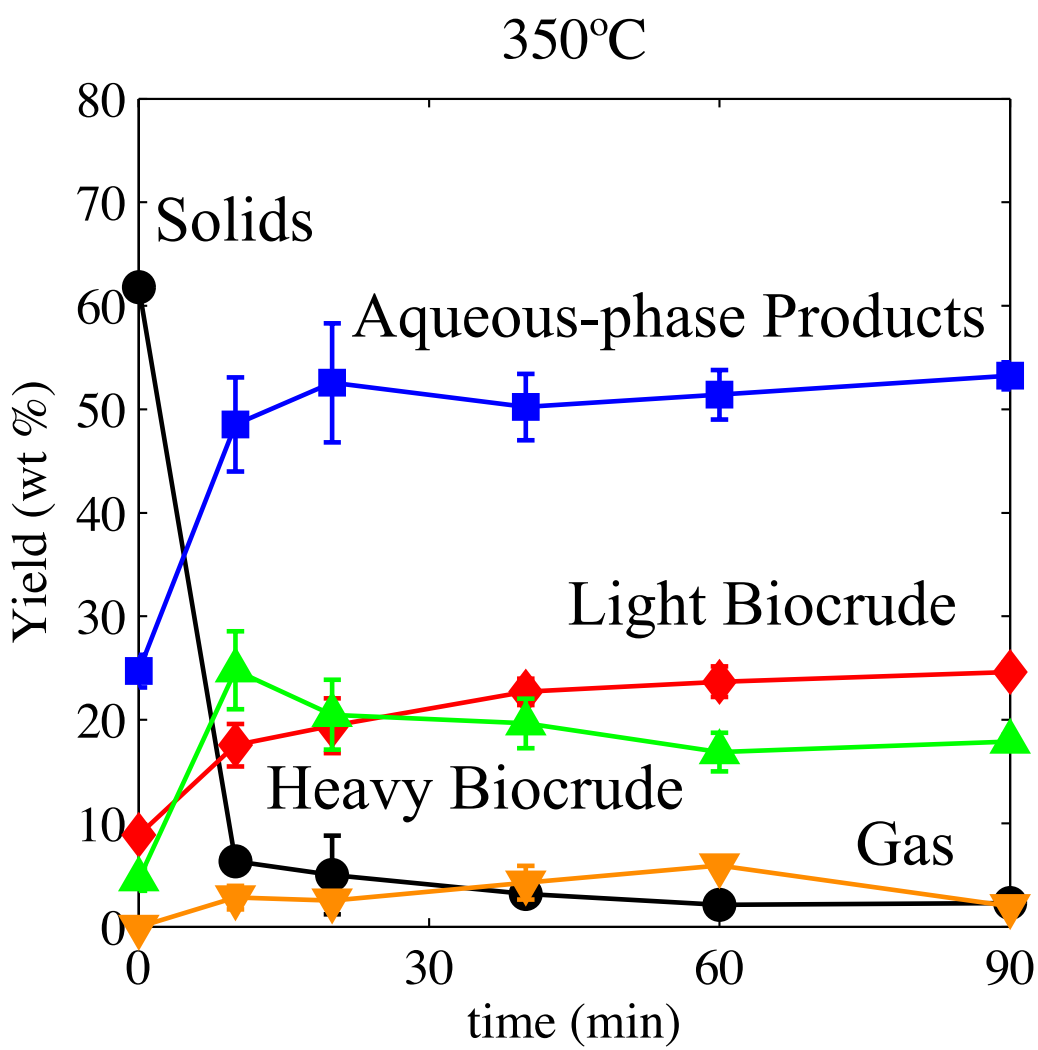
Total Ion Chromatogram of Bio-Crude

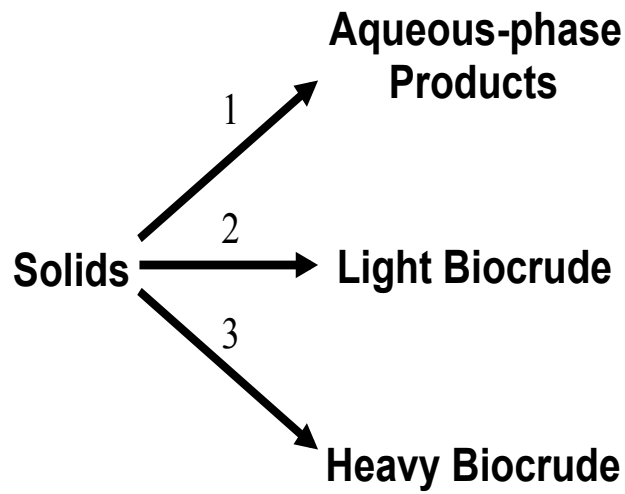


C & N distributions at 20 min



Reaction Network?

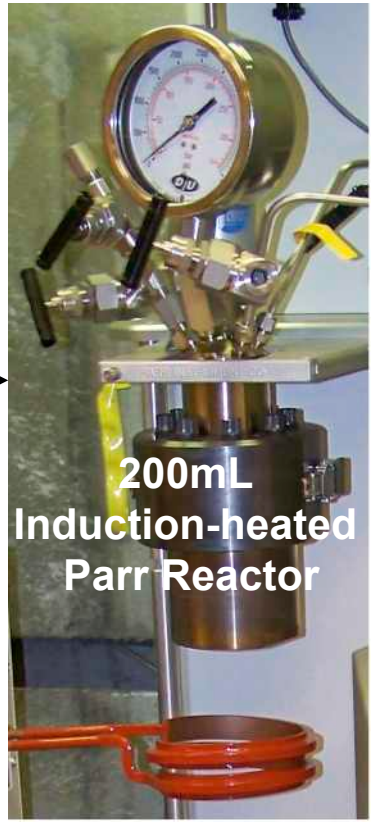


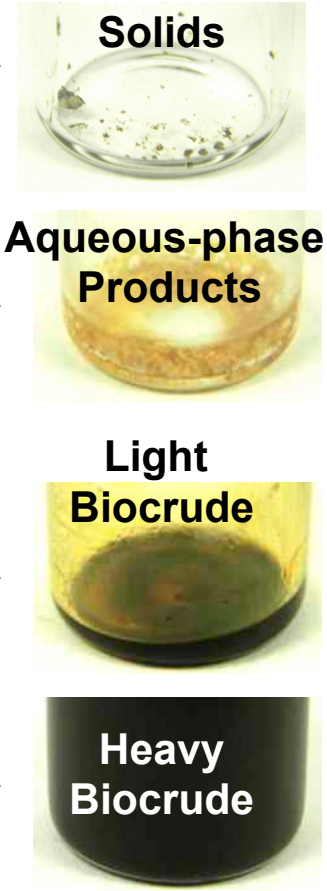


P. Valdez, et al., Hydrothermal Liquefaction of *Nannochloropsis* sp.: Systematic study of process variables and analysis of the product fractions, Biomass and Bioenergy, (2012)

Reactions of Intermediate Products

350°C, 40min
15 wt % slurry





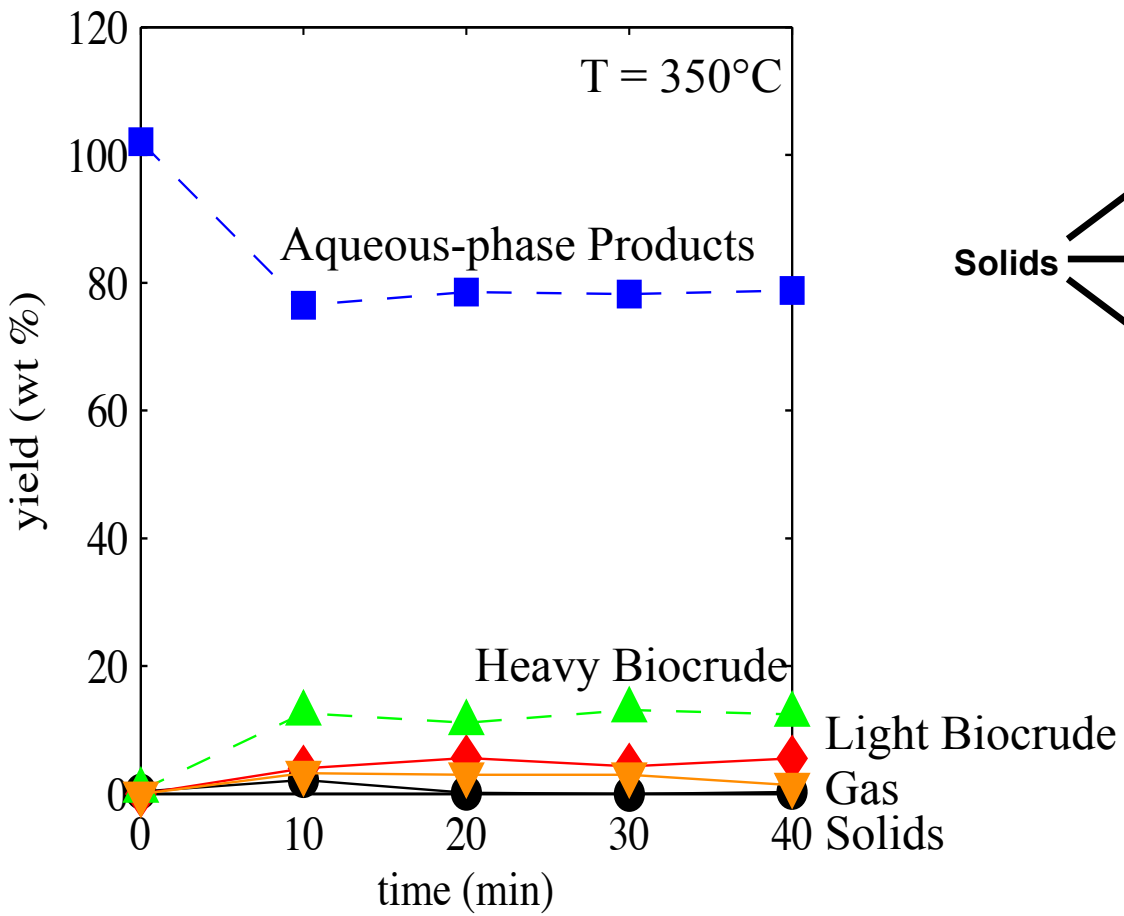
350°C, 10-40min
5 wt % loading

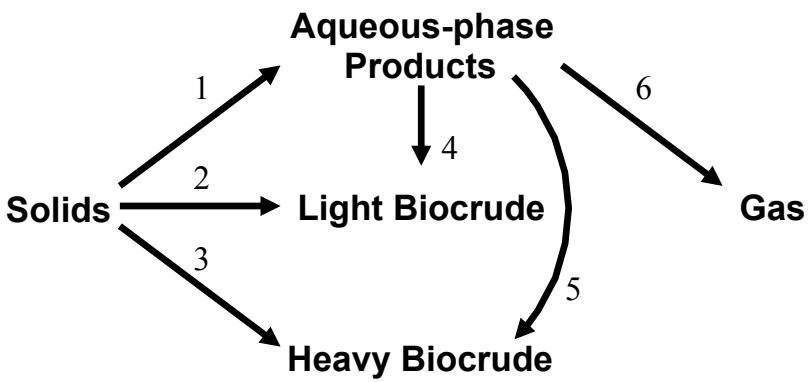
4mL
Swagelok
Reactor

Product
Workup

Reaction of Aqueous-phase Products

- Aqueous-phase produces Light and Heavy Biocrudes and relatively large amounts of CO_2 (~3 wt %)

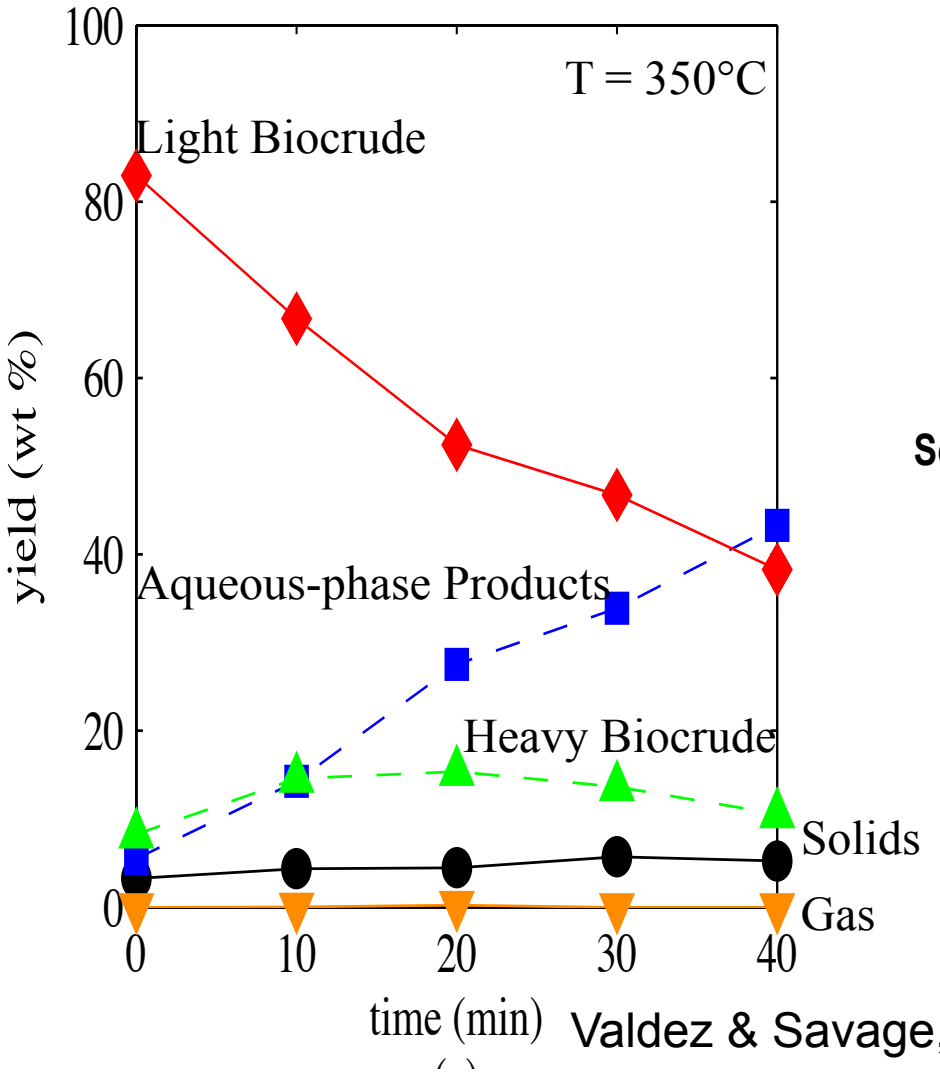


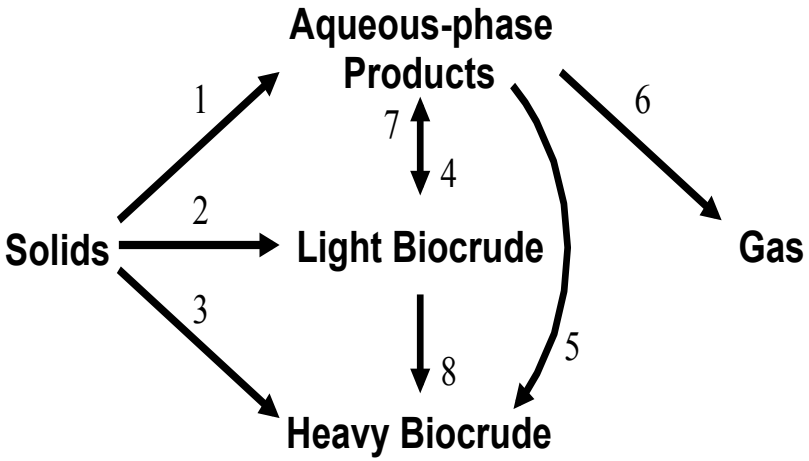


Valdez & Savage, *Algal Research*, under review

Reaction of Light Biocrude

- Light Biocrude produces Aqueous-phase and Heavy Biocrude

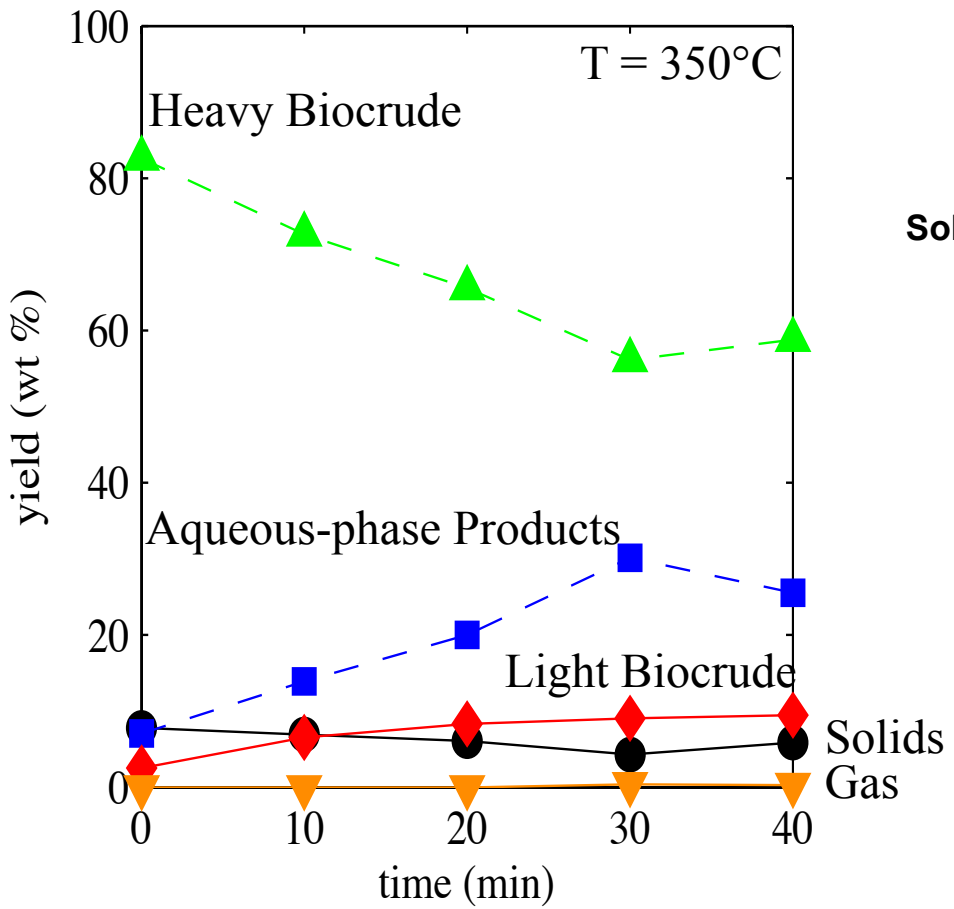


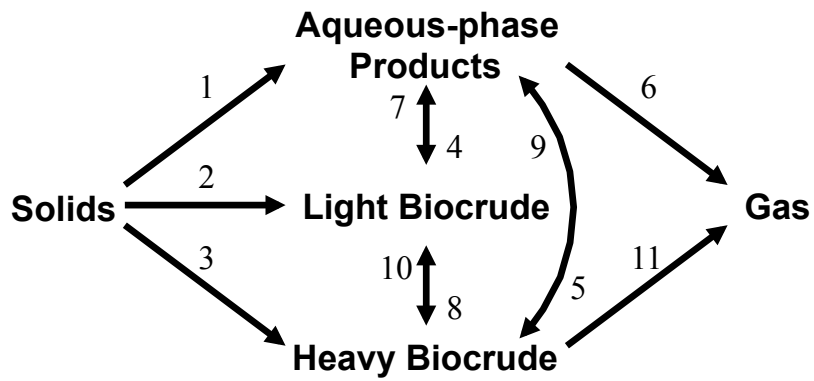


Valdez & Savage, *Algal Research*, under review

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

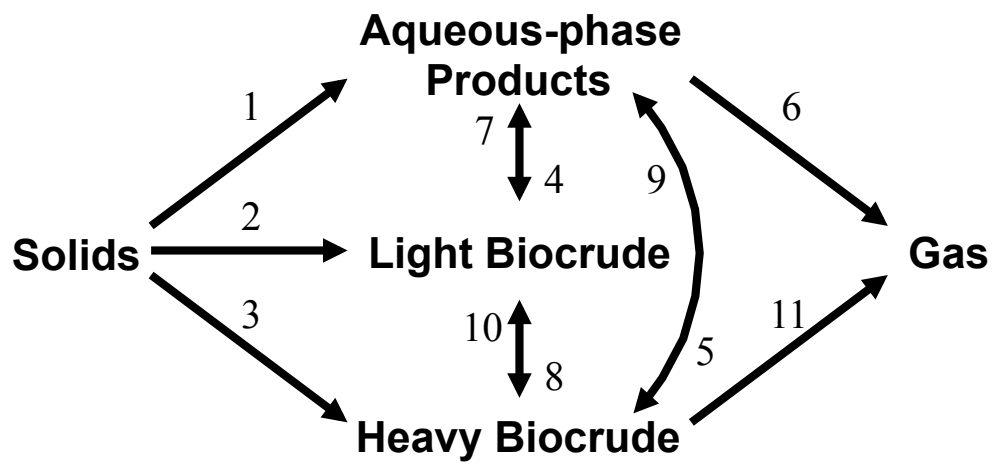
- Write & solve governing equations
  - x_i = mass fraction of each product
  - 1st order kinetics

$$\frac{dx_i}{dt} = \sum_i \sum_j \nu_{ij} k_j x_i$$

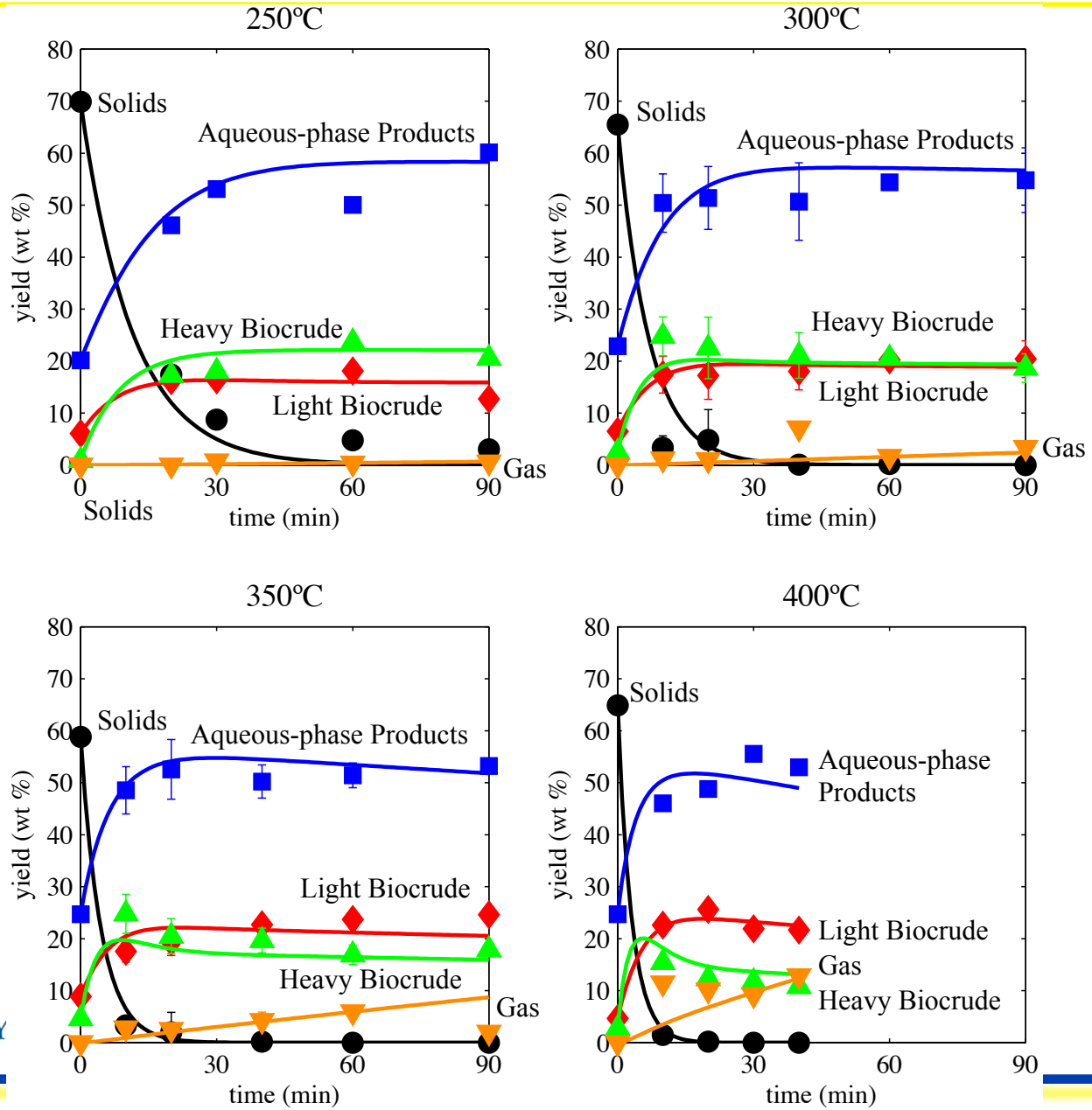
- Estimate rate constants by minimizing objective function

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

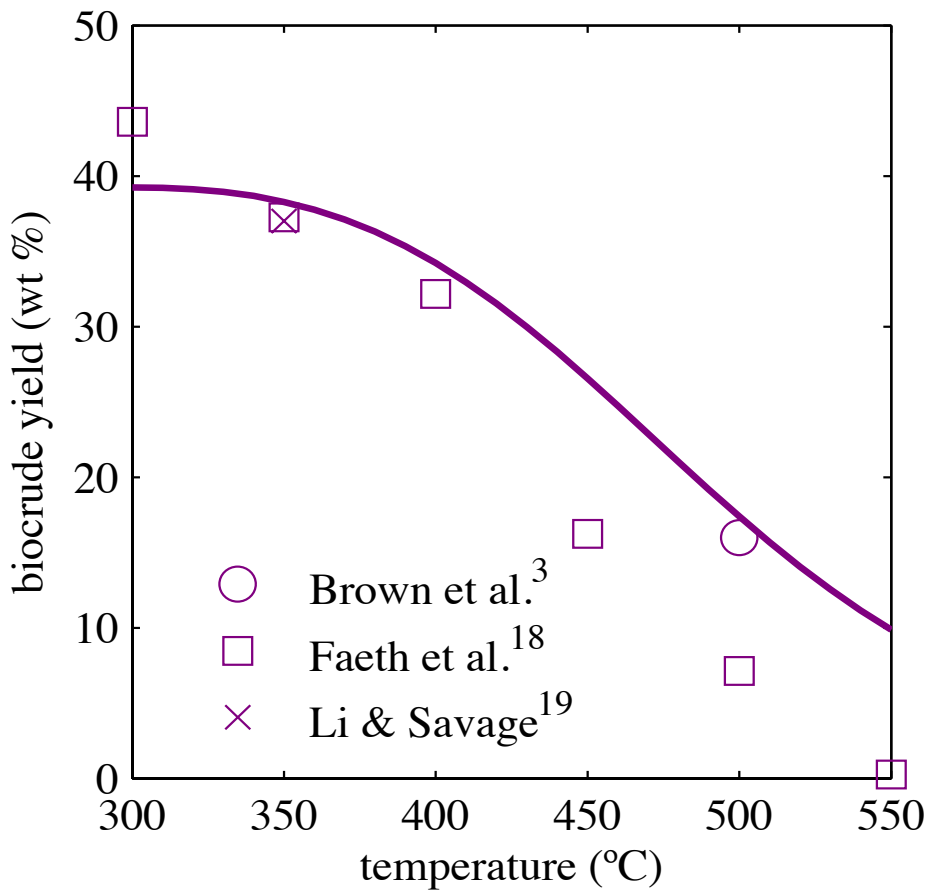
- Used MATLAB, Constrained, non-linear multivariable function



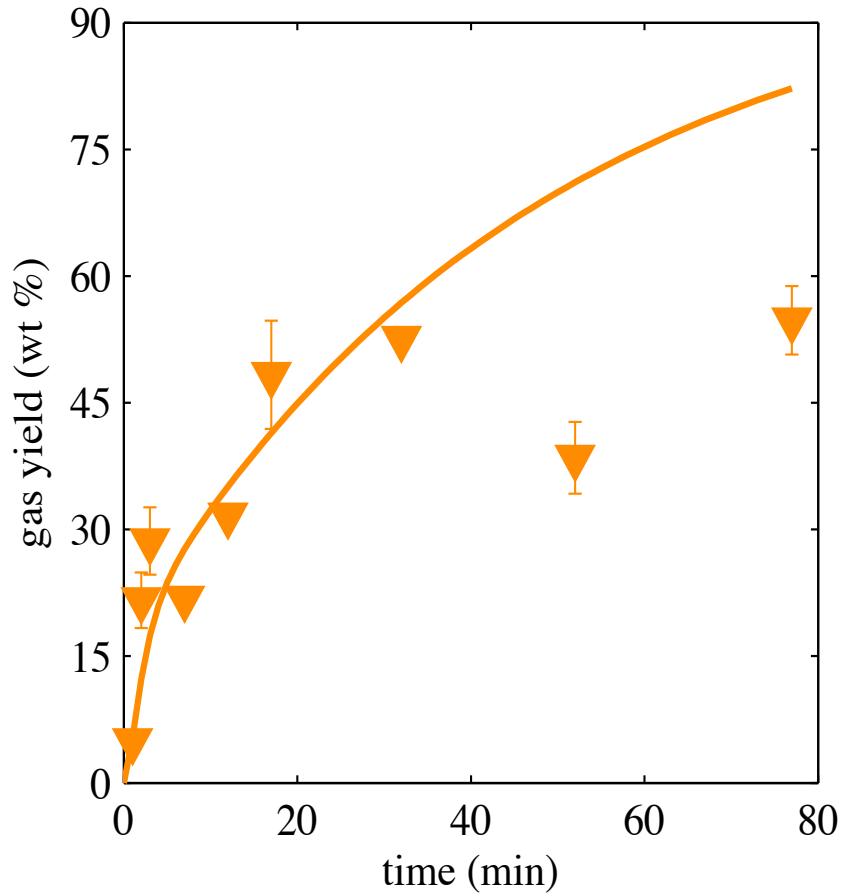
Model & Exptl. Results for HTL



Model Predictions



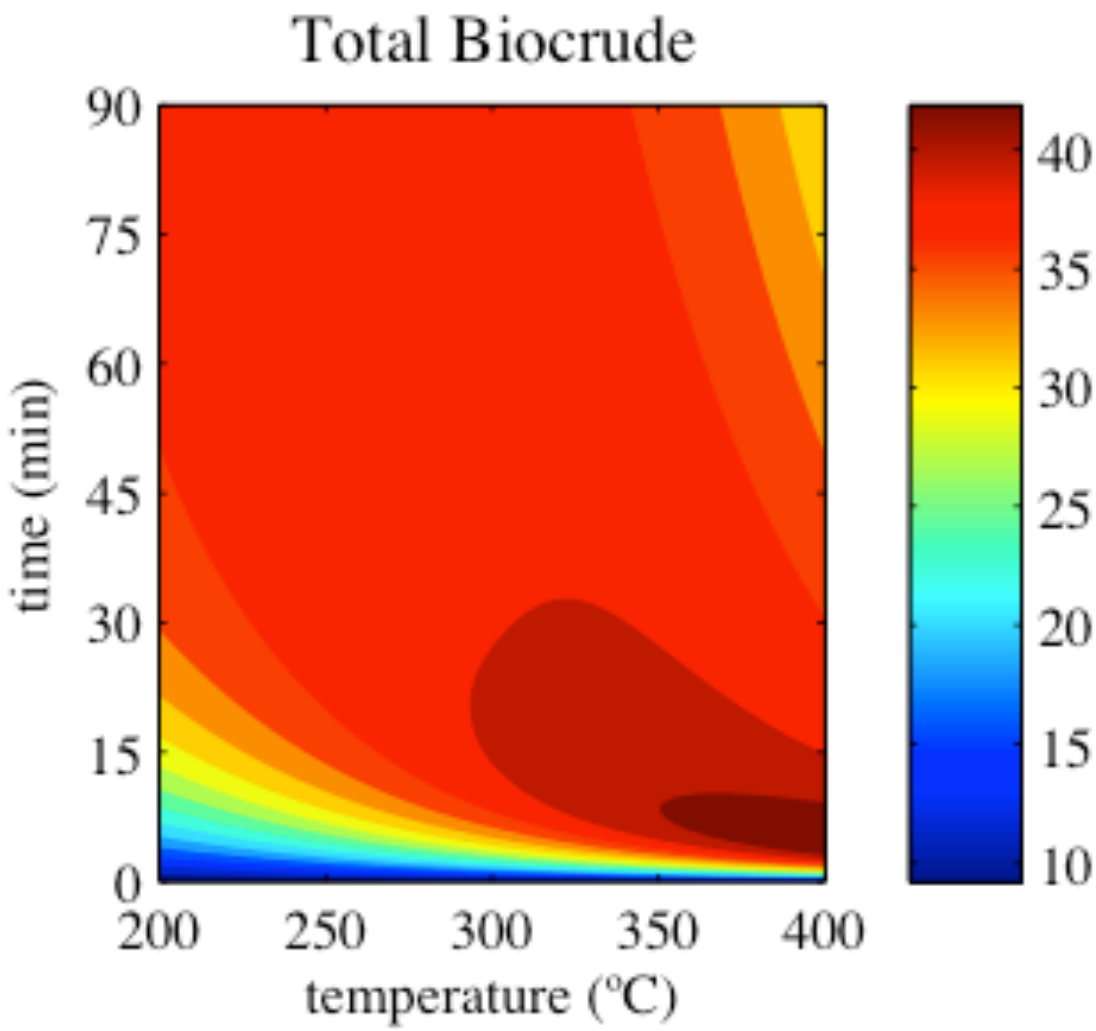
Biocrude yields from liquefaction of *Nannochloropsis* sp. at 60 min



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

Valdez & Savage, *Algal Research*, 2013

Model Predictions



High temp, short time gives highest biocrude yields

Rapidly heat to high temperature

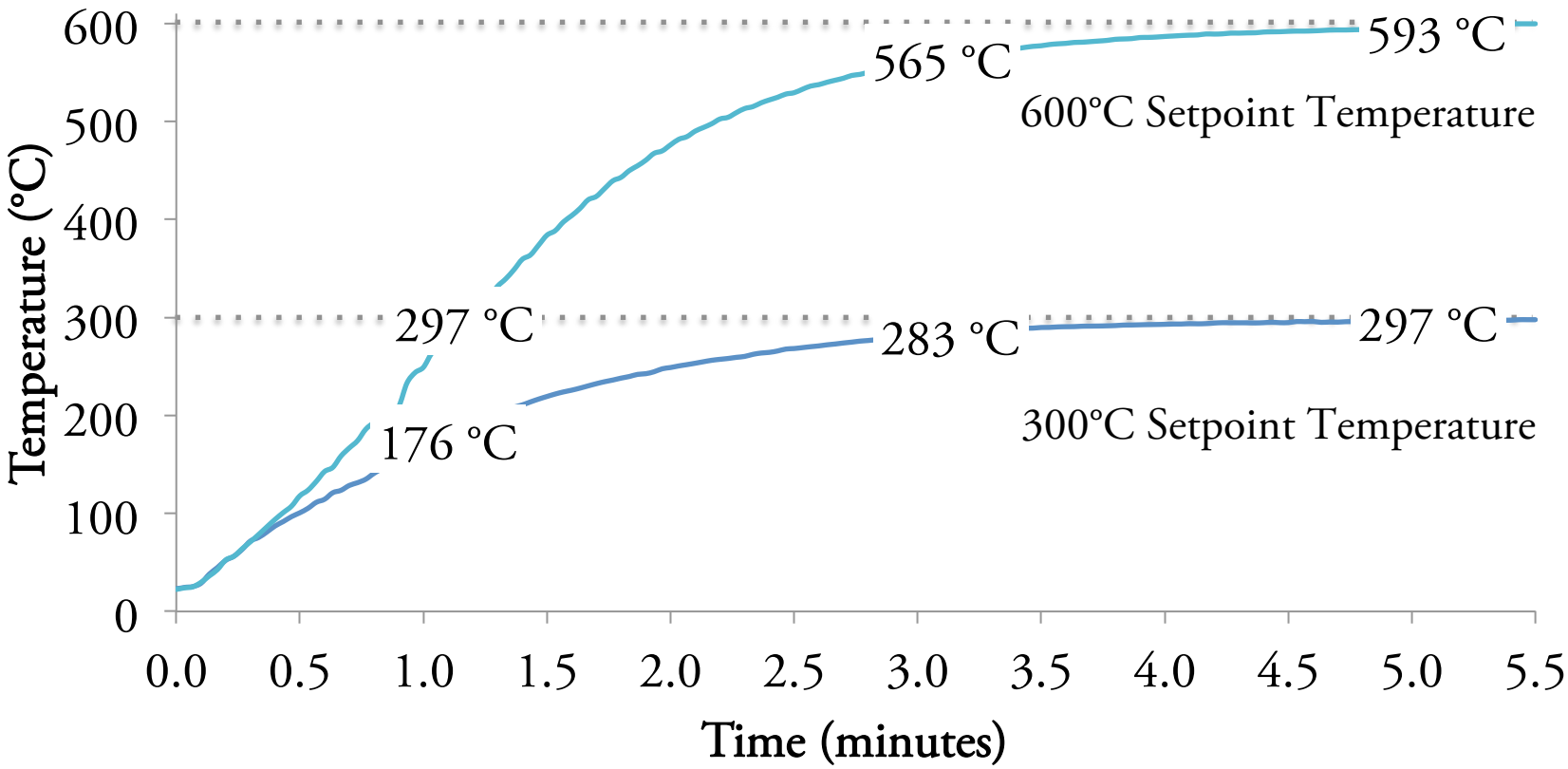
"Fast" liquefaction

Valdez & Savage, *Algal Research*, 2013

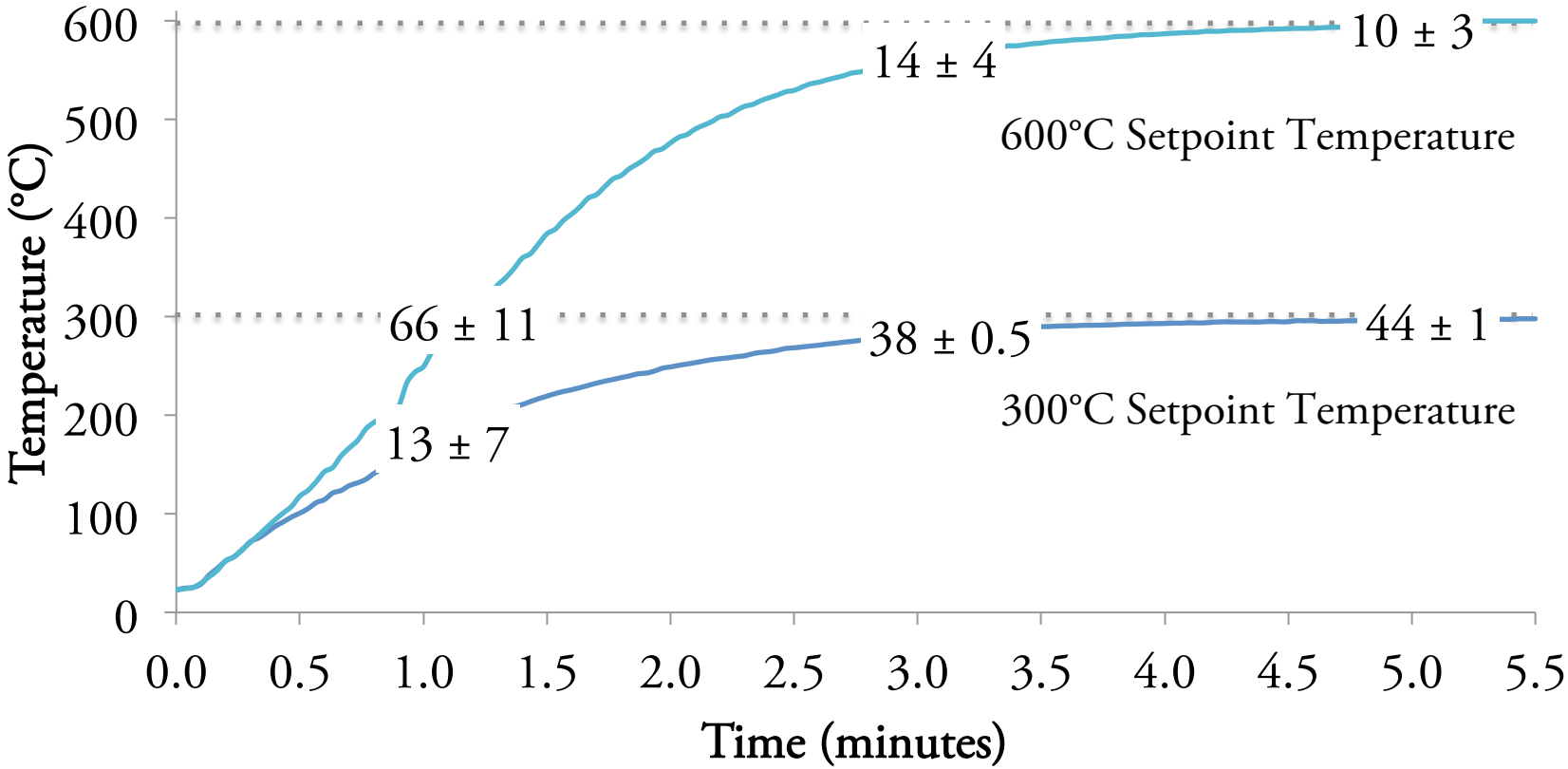
Fast Hydrothermal Liquefaction

- *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

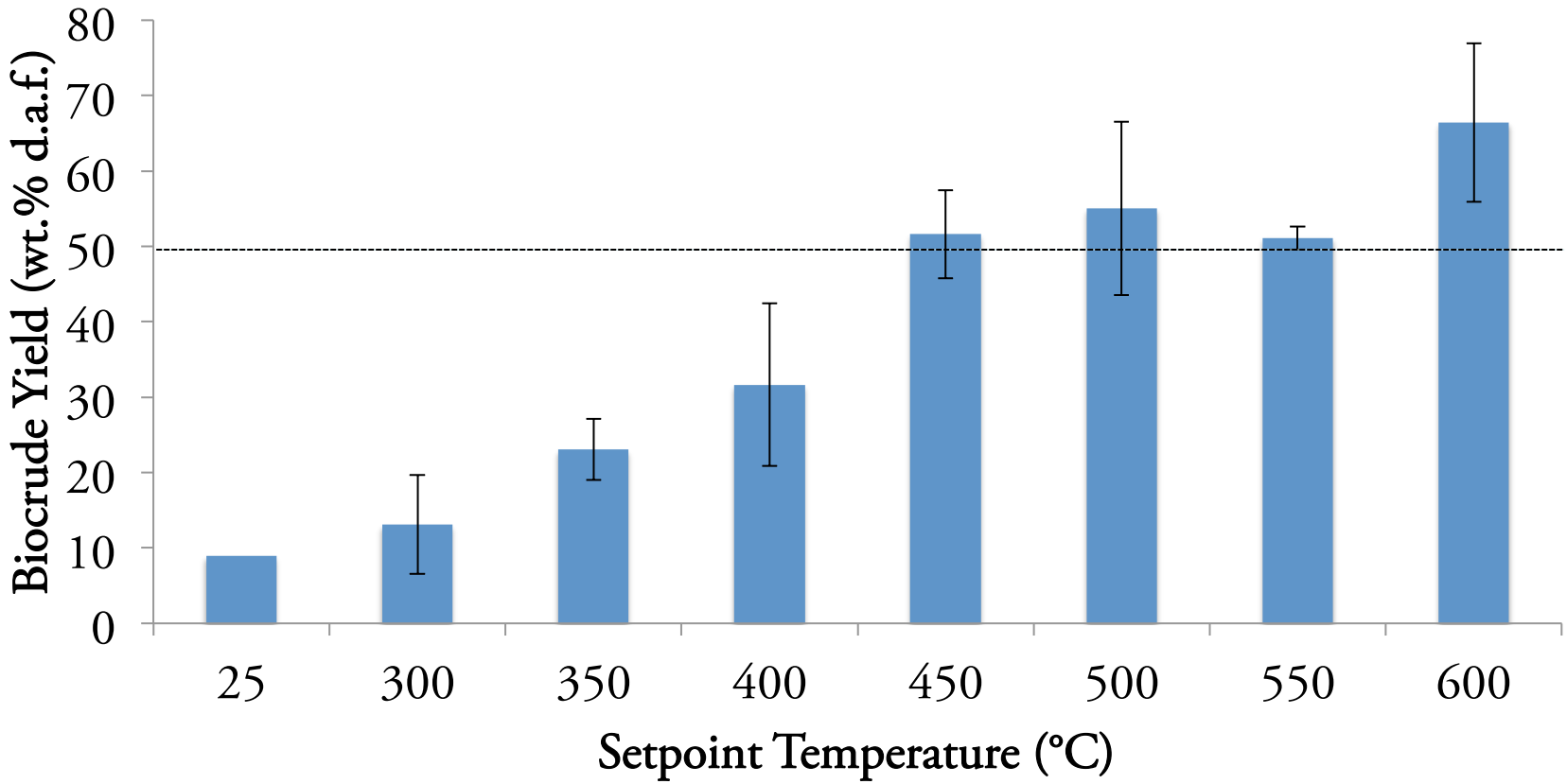


Total Biocrude Yield (wt.%)



Uncertainty given is standard deviation

Total Biocrude Yields - 1 minute



Faeth, Valdez & Savage, *Energy & Fuels*, 2013

Reaction Ordinate

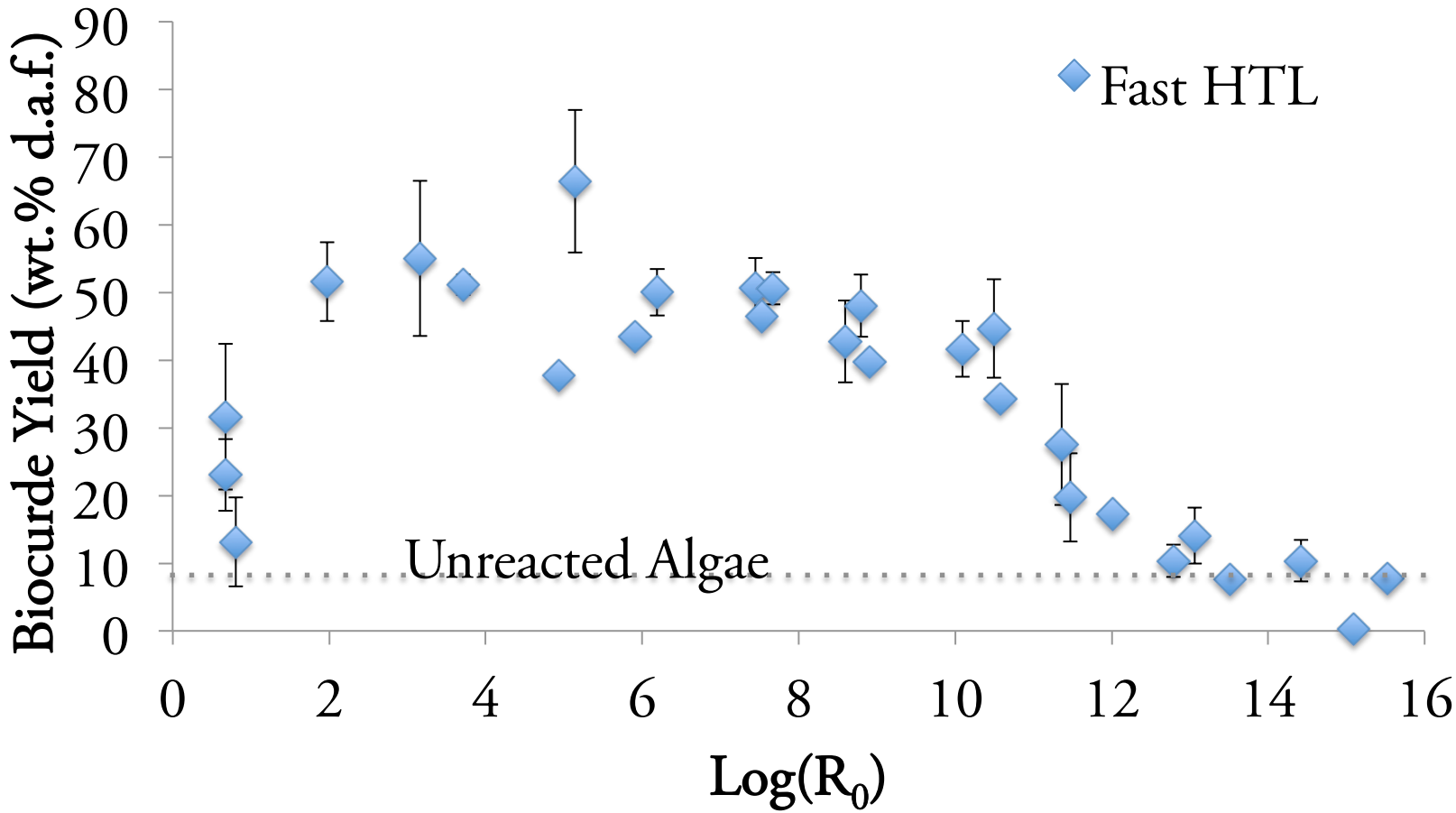
- Severity index that combines effects of time and temperature[1]

$$R_0 = \int_0^t exp\left(\frac{T(t)°\mathrm{C} - 100°\mathrm{C}}{14.75°\mathrm{C}}\right)dt$$

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

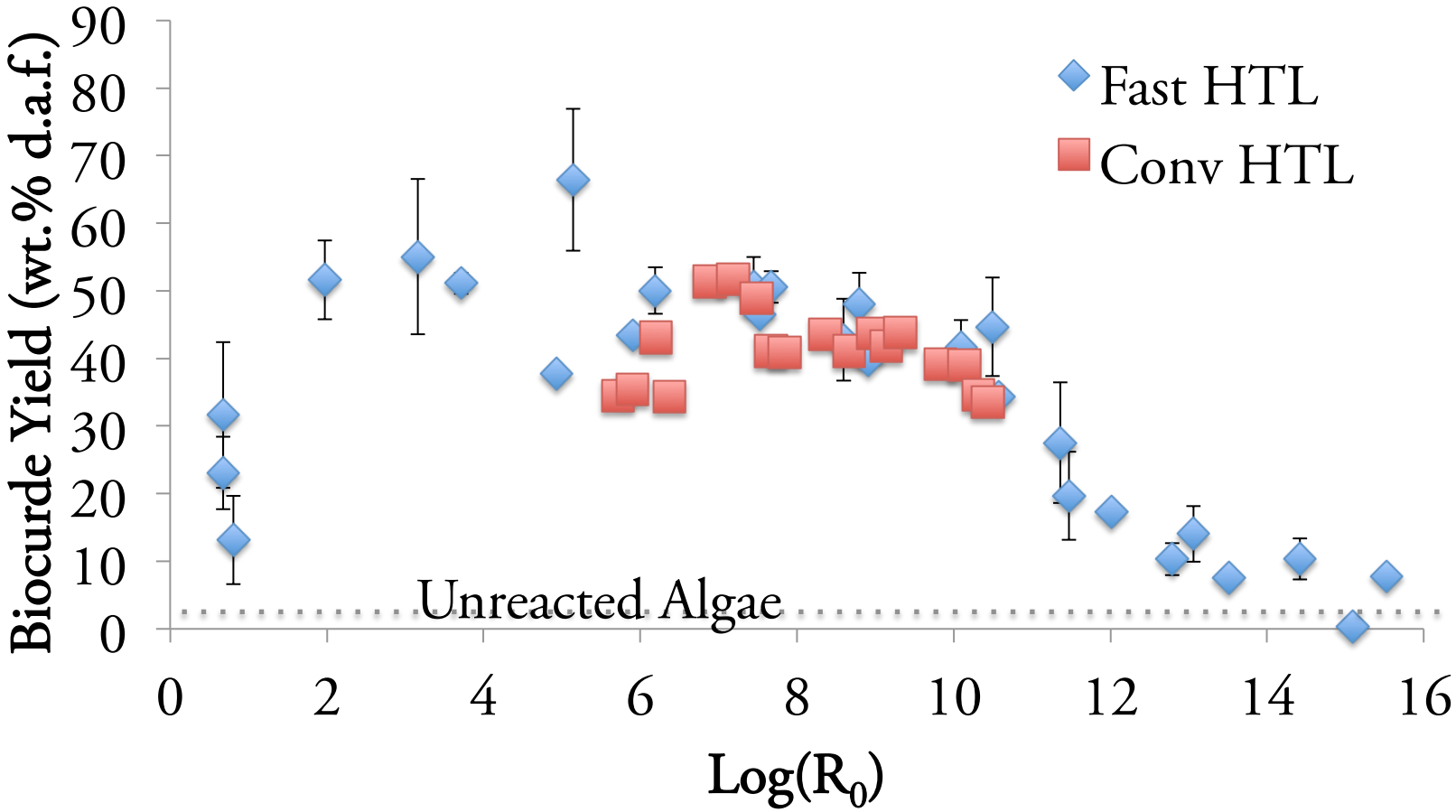
[1] T. Rogalinski, T. Ingram, and G. Brunner, *The Journal of Supercritical Fluids*, 2008, **47**, 54–63.

Total Biocrude Yield with R_0



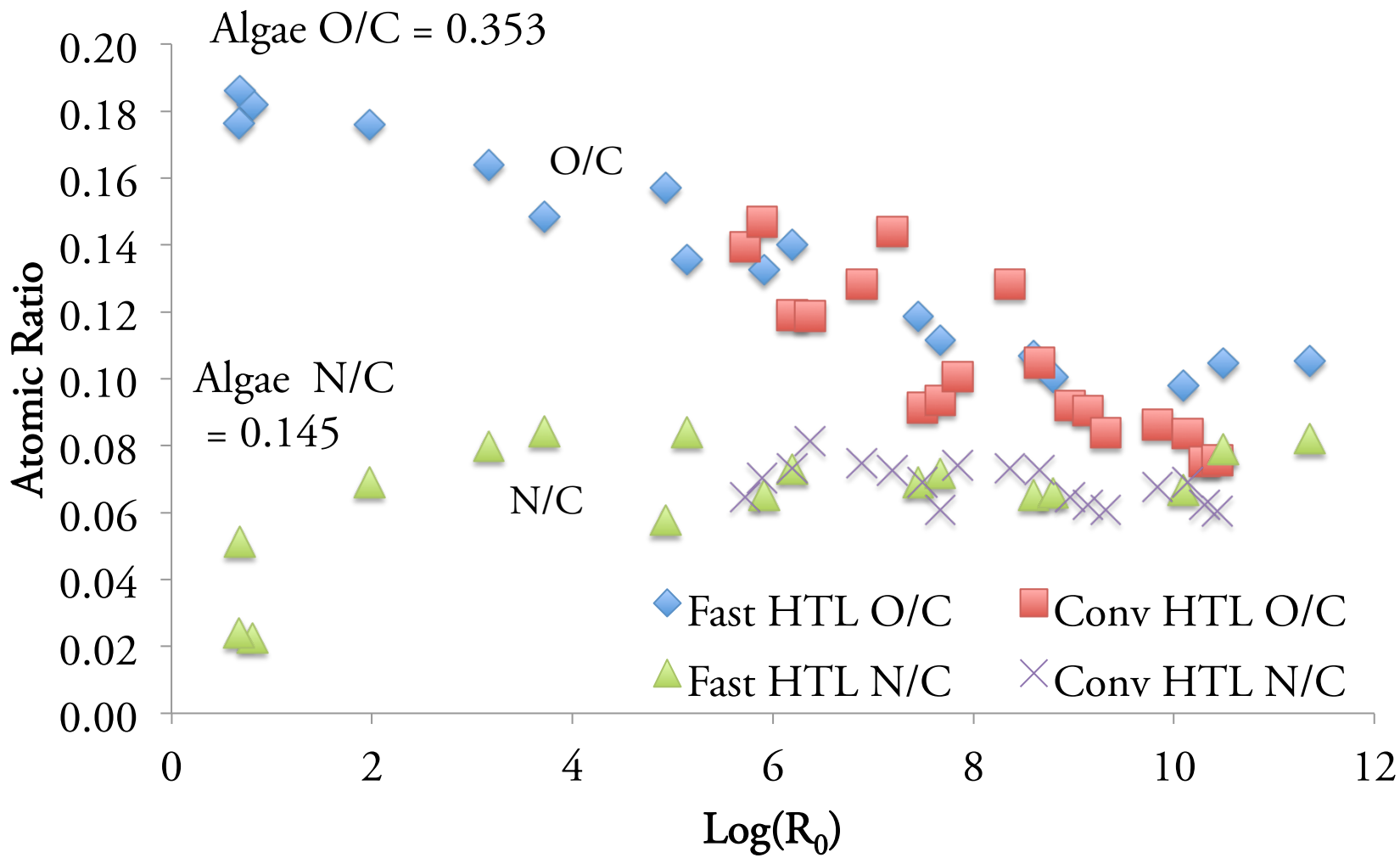
Faeth, Valdez & Savage, *Energy & Fuels*, 2013

Total Biocrude Yield with R_0



Conv. HTL Data from Valdez et al., *Biomass and Bioenergy*, 2012

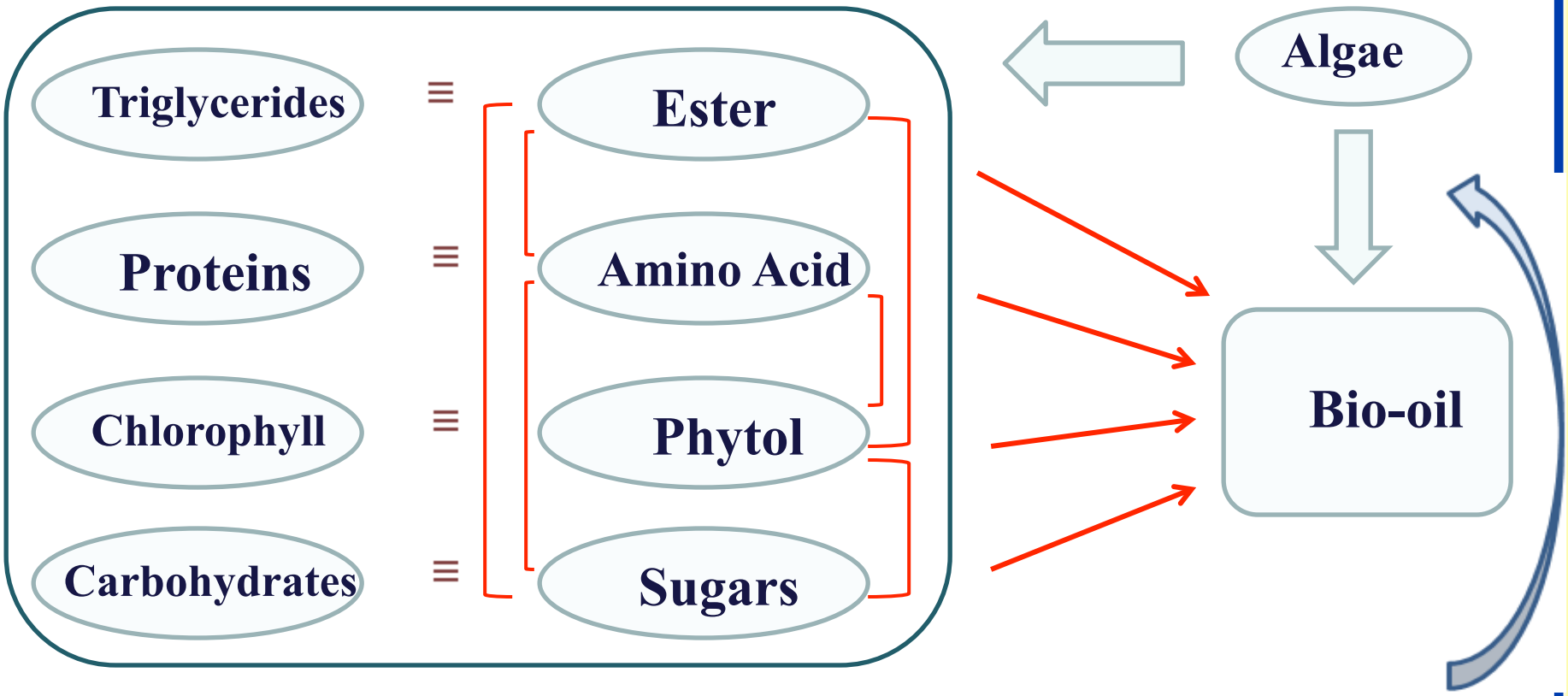
Biocrude O/C, N/C Ratios



Faeth, Valdez & Savage, *Energy & Fuels*, 2013

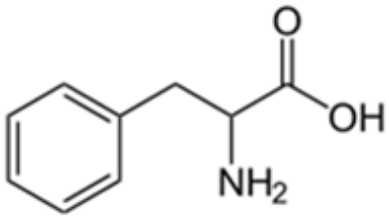
Model Compound Approach

- Chemical details likely to be obscured starting with algae directly



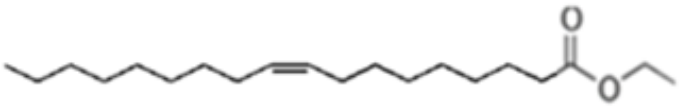
Specific ⇨ **How do model compounds react individually and interact with each other in HTW?**

Phenylalanine



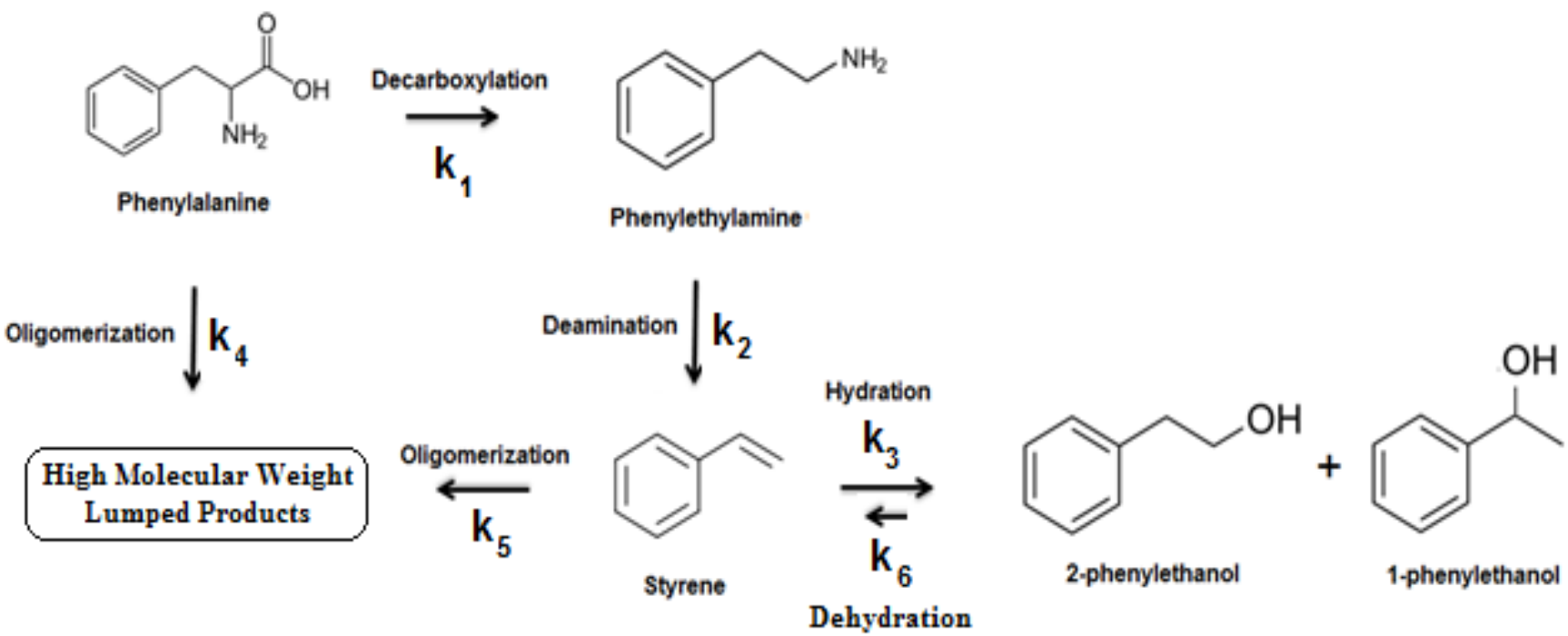
Protein

Ethyl Oleate



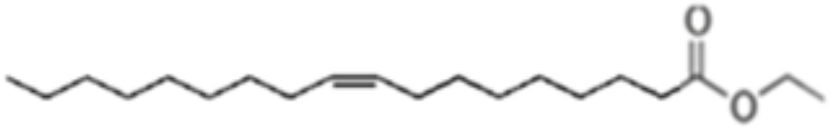
Lipids

Phenylalanine Reaction Pathway

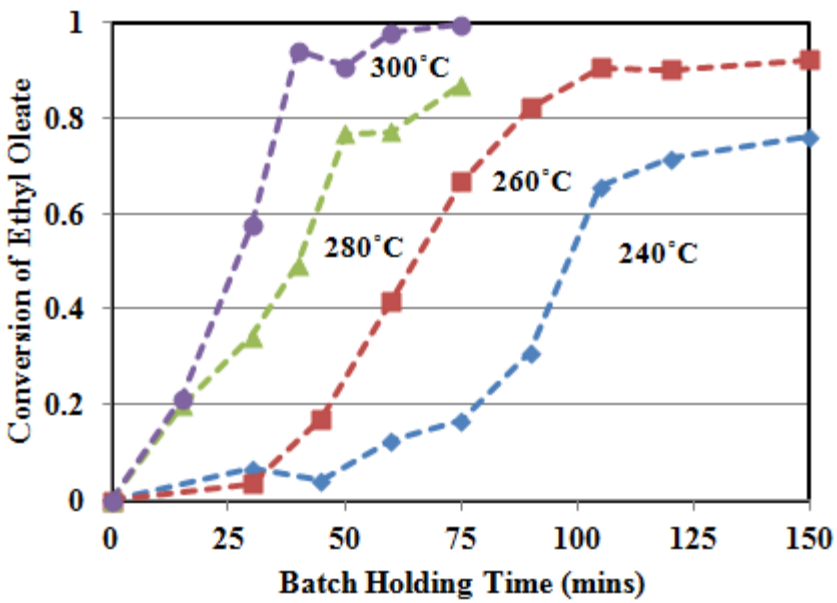


[Changi et al., *ChemSUSChem* (2012)]

Ethyl Oleate Hydrolysis



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

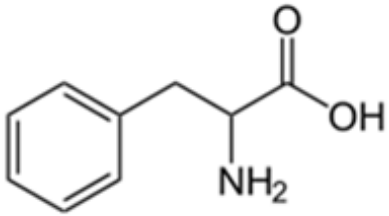


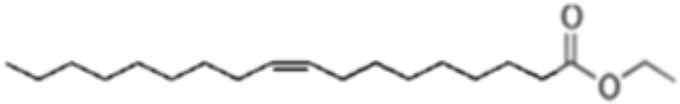
Effect of Added Oleic Acid

$\frac{\text{Moles}_{\text{Oleic Acid}}}{\text{Moles}_{\text{Ethyl Oleate}}}$	Conversion (240˚C, 30 minutes)
0	0.07 ± 0.03
0.25	0.27 ± 0.07
0.5	0.41 ± 0.05
1	0.61 ± 0.09

[Changi et al., *Ind.Eng.Chem.Res.* (2011)]

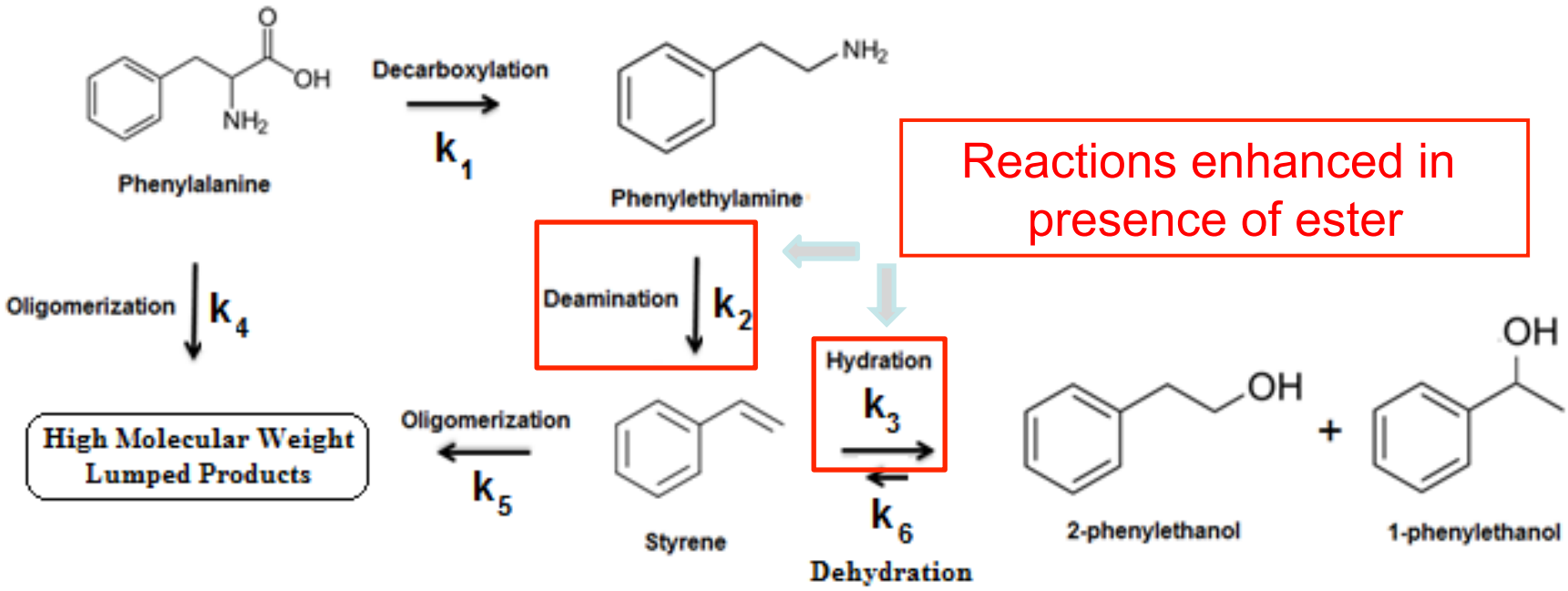
Phenylalanine + Ethyl Oleate





Effect of Adding Ethyl Oleate

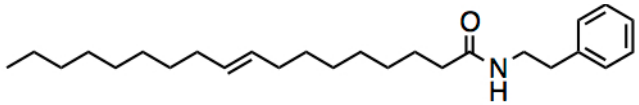
- Phenylethylamine (primary product) yield decreases with added ester
- Styrene, 2-phenylethanol (2° products) yields increase with added ester



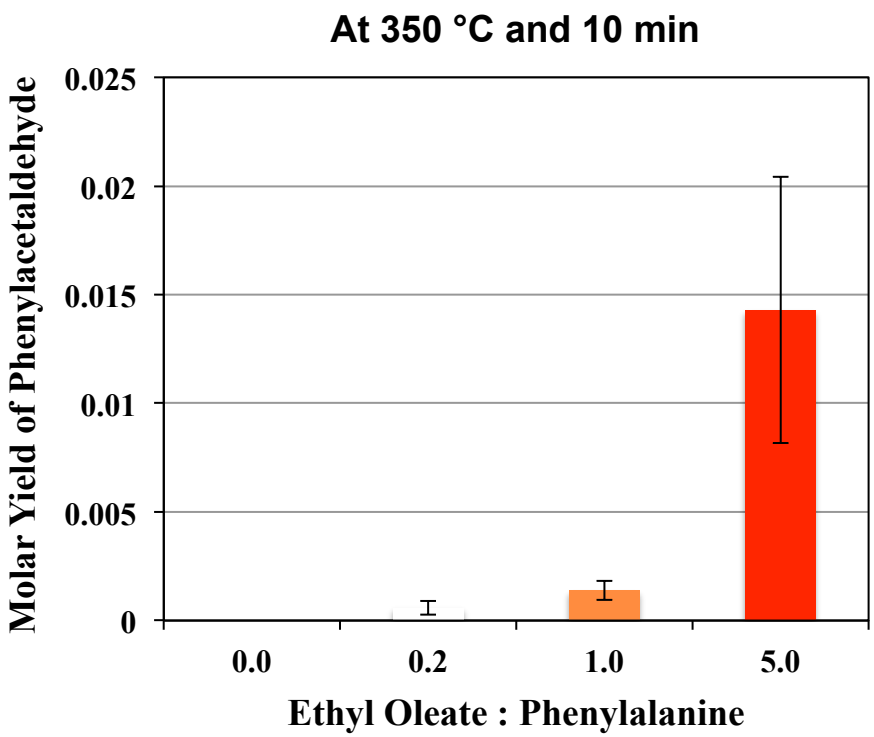
[Changi et al., *ChemSUSChem* (2012)]

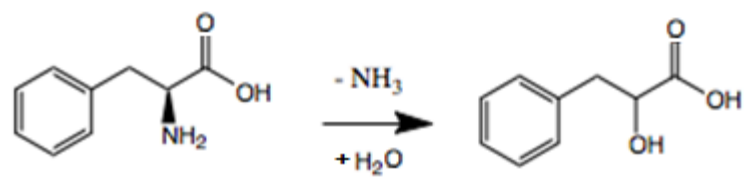
Effect of Adding Phenylalanine

- Formation of new products - oleic acid amides, phenylacetaldehyde



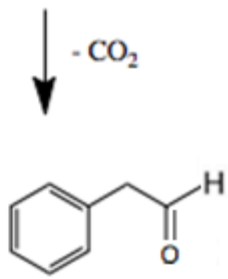
N-phenylethyl-9-octadecenamide





Phenylalanine

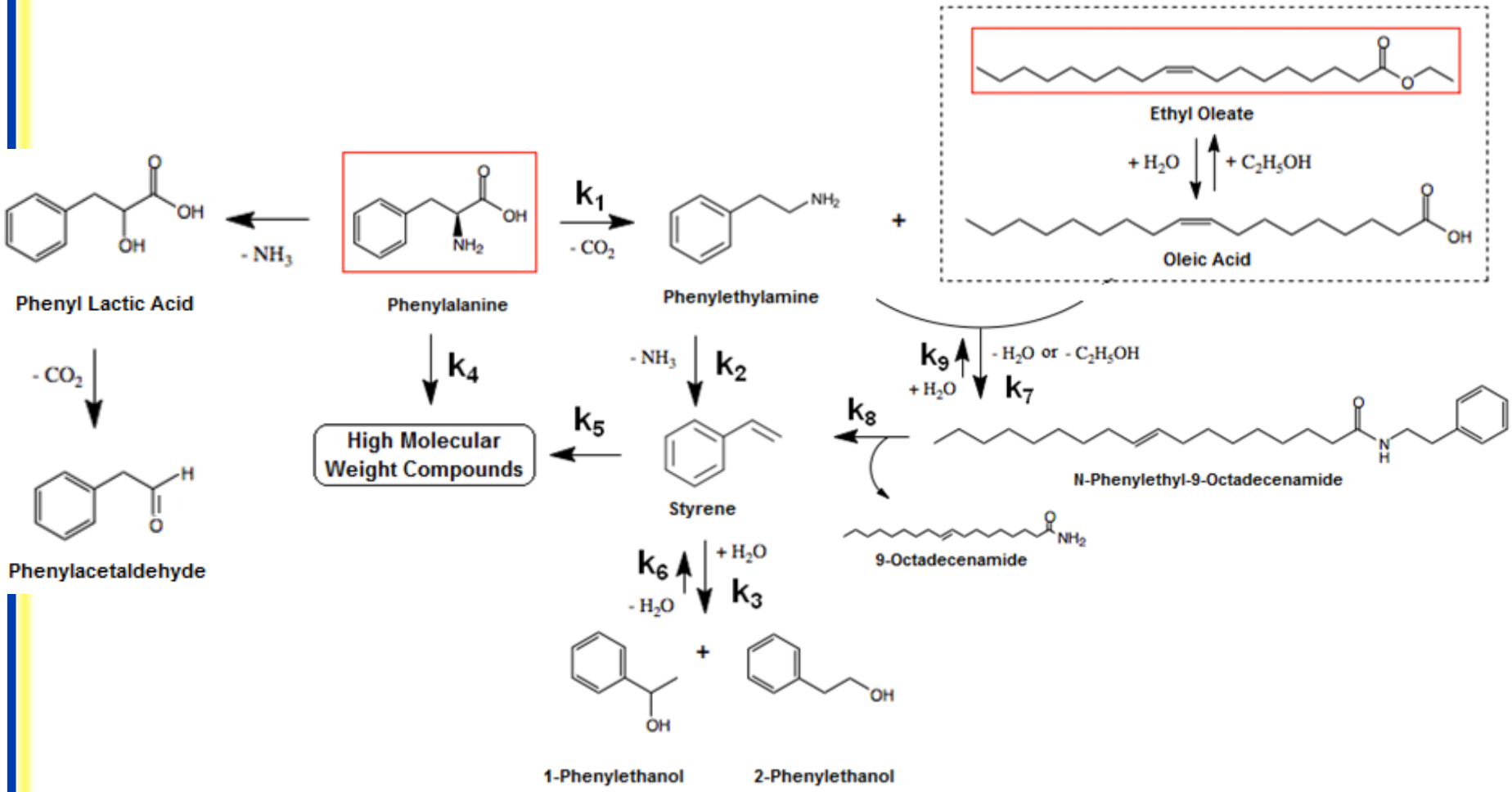
Phenyl Lactic Acid



Phenylacetaldehyde

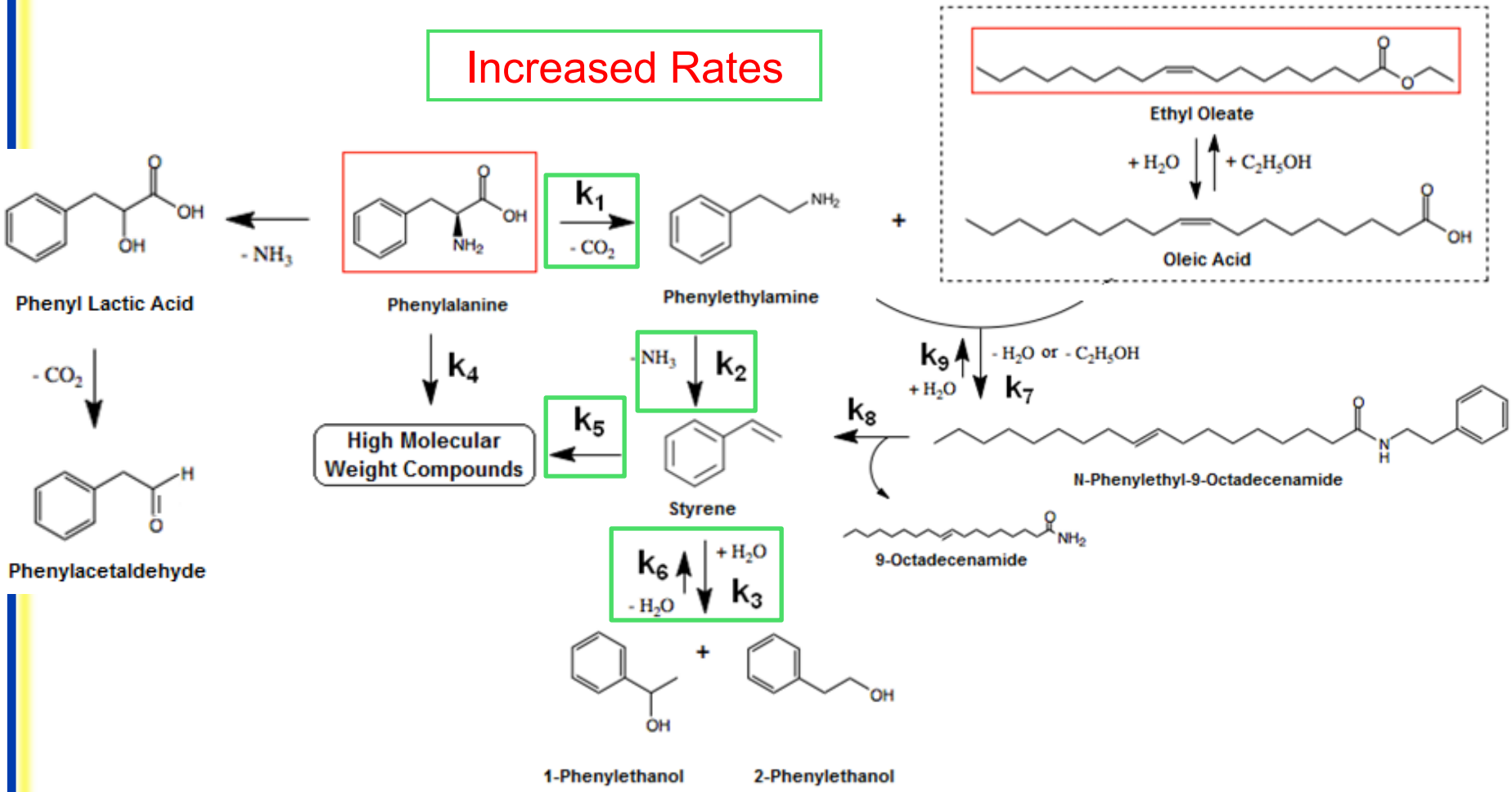
[Changi et al., *ChemSUSChem* (2012)]

Reaction Network for Binary System



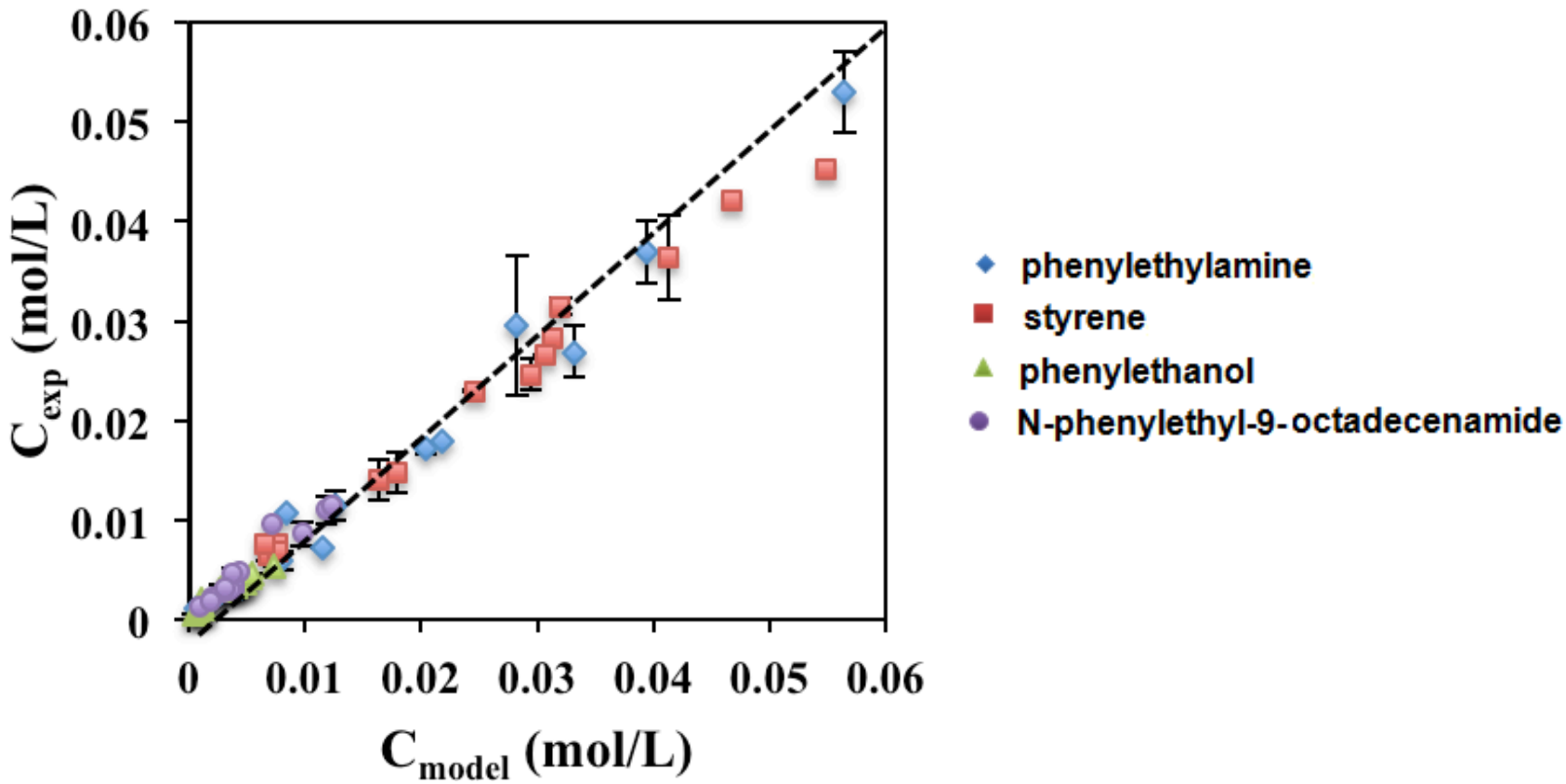
[Changi et al., *ChemSUSChem* (2012)]

Reaction Network for Binary System



[Changi et al., *ChemSUSChem* (2012)]

Parity Plot for Binary System



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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