Algal Biofuels

The Washington Bioenergy Research Symposium

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November 8, 2010

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PNNL-SA-76122

Outline

- PNNL
- Intro: promise and challenge of algal biofuels
- Industry and government support
- NAABB
  - Participants & Teams
  - General research aims
  - PNNL research examples
- PNNL research on macroalgae

PNNL

Operated by Battelle for the US Dept. of Energy

- **~4800 employees**
- **~50% S&E's**
- **Office of Science, multi-program laboratory**

- **Three Research Directorates**
  - **EED: Energy & Environment**
  - **FCSD: Fundamental & Computational Sciences**
  - **NSD: National Security**
- **BSEL (Bioproducts, Sciences & Engineering Lab**
  - **WSU Tri-Cities and PNNL shared facility**

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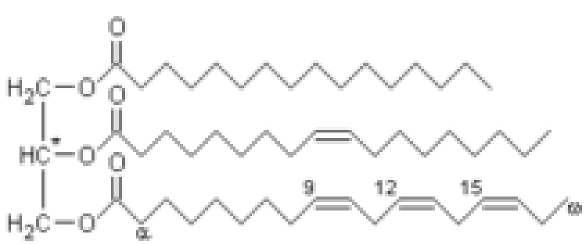
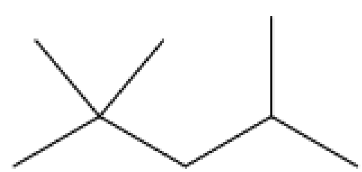
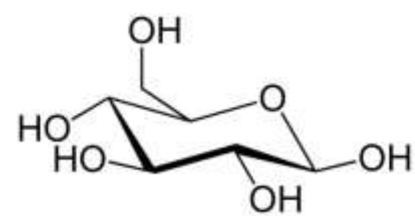
Algal Biofuels: The Promise

- Primary producers
  - Higher productivity than terrestrial plants
  - CO_2 consumers -- potential green house gas neutral processes
- Could (must) use non-arable land
- Could use non-potable water: wastewater, produced water, saline aquifer, ocean, etc.
- Could use “waste” nutrient sources (sewage, feedlot, agricultural runoff)
- Produce lipids; more like hydrocarbons than sugars



Triacylglyceride (TAG)


Isooctane



Glucose

Algal Biofuels: The Promise

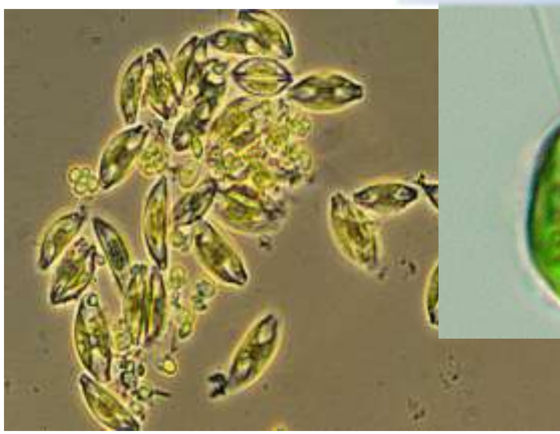
Why now?

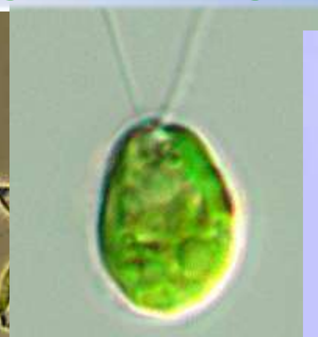
- Genomics era biotechnology tools and resources
  - ≥ two dozen eukaryotic algal genome projects: green algae, diatoms, red algae
  - ≥ three dozen prokaryotic algal genome projects
  - Genomes are resources for understanding the biology of algae growth, photosynthesis and lipid production
  - Tools to engineer better biofuels production strains from knowledge gained
- Algal biodiversity yet to be explored
  - High throughput isolation and culturing (cell sorters)
  - High throughput lipid screening tools available

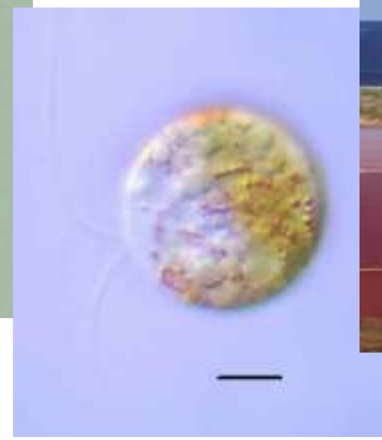
Biodiversity

Tens of thousands of algal species

Eukaryotic Microalgae: green algae, diatoms, etc.







Cyanobacteria; prokaryotic microalgae

Macroalgae; seaweeds

Comparison of Oil Yields from Biomass Crops

Crop	Oil Yield (L/ha/yr)
Soybean	450
Camelina	600
Sunflower	950
Jatropha	1900
Oil Palm	5900
Microalgae (low estimate)**	9300
Microalgae (high estimate)**	61000

*Table adapted from Chisti, 2007 as seen in the Algal Biofuels Roadmap, 2010

**Estimated in the Algal Biofuels Roadmap, 2010

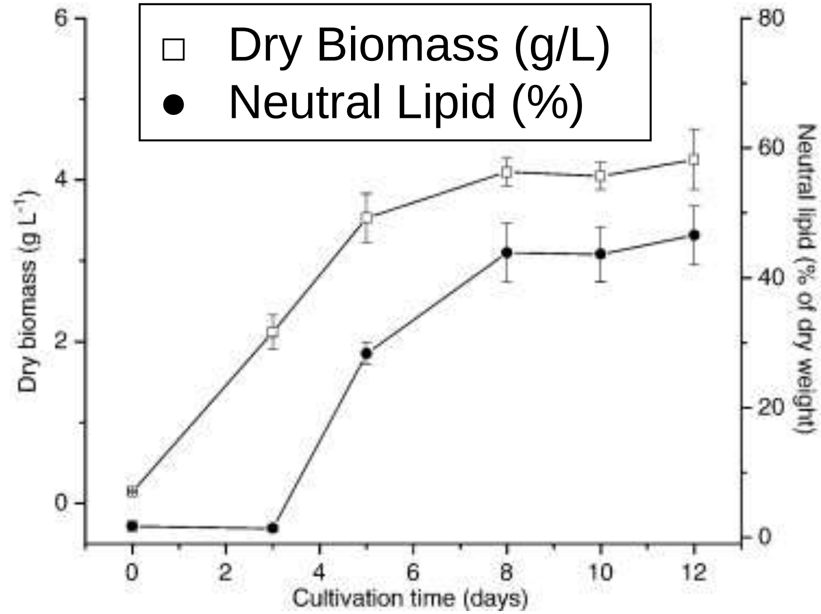
Theoretical numbers

Algal Biofuels: The Challenges

- Consistently high biomass and lipid **productivity** at scale
- Lipid production and growth are often uncoupled
- **Water**
- **Nutrient** sources (CO_2, N, P)
- Low culture density (~0.05% solids) challenge for **harvesting**
- Energy efficient, environmentally friendly lipid **extraction**
- Conversion to infrastructure compatible **fuels**
- Need various **co-products** from the lipid extracted algae (LEA)
- **Site-selection** bound by many parameters: slope, land use, water, nutrients, climate, light, etc.

Fig. 9
Growth & Lipid Accumulation in *Chlorella vulgaris*

Chen et al. 2009, J of Microbiol Methods **77**:41–47



in short, we need an **economical & sustainable process**

Private Investment
Algal Industry Explosion

(non-exhaustive list)

Predating the Current Algal Bloom (higher value products)

- Cyanotech
- Martek
- A few others

Renewed Interest in Algal Biofuels (since ~2005)

- Targeted Growth
- Solix Biofuels
- Sapphire Energy
- Solazyme
- Seambiotic
- Phycal
- Live Fuels
- Aurora Biofuels
- Inventure Chemical
- Kai BioEnergy
- Genifuel
- Imperium Renewables
- AXI
- HR Biopetroleum
- Diversified Bioenergy
- Eldorado Biofuels

Government Investment
DOE-EERE-OBP* Support

- *Historic*: Aquatic Species Program, 1978-96, $25M
- Algal workshop, Dec 2008
- Algal Roadmap, June 2010
- NAABB, $49M (+ $18M industry cost share) algal consortium, awarded Jan 2010
- Three additional small consortium awards totaling $25M, May 2010
  - Cellana LLC, Hawaii
  - CAB-Comm, California
  - SABC, Arizona

**Department of Energy, Energy Efficiency and Renewable Energy Office of the Biomass Program*

- **National Alliance for Advanced Biofuels and Bioproducts (NAABB)**
  - Institutional Lead: The Donald Danforth Plant Science Center
  - Leader: José Olivares
  - Funds: Federal ~$49M ; Industry Cost Share ~$18M
  - Develop the science and technology necessary to significantly increase production of algal biomass and lipids, efficiently harvest and extract algae and algal products, and establish valuable conversion routes to fuels and co-products.




NAABB Partnership

Prime Contractors: 15 Companies, 15 Research Institutions

Lead Institution

- Donald Danforth Plant Science Center

National Laboratories

- Los Alamos National Laboratory
- Pacific Northwest National Laboratory

Universities

- Brooklyn College
- Colorado State University
- New Mexico State University
- Texas AgriLife Research (TAMU)
- Texas A&M University System
- University of Arizona
- University of California Los Angeles
- University of California San Diego
- University of California Davis
- University of Washington
- Washington University, St. Louis

Industries

- AXI
- Allied Minds
- Catilin
- Diversified Energy
- Eldorado Biofuels
- Genifuel
- HR Biopetroleum
- Inventure
- Kai BioEnergy
- Palmer Labs
- Pratt & Whitney
- Solix Biofuels
- Targeted Growth
- Terrabon

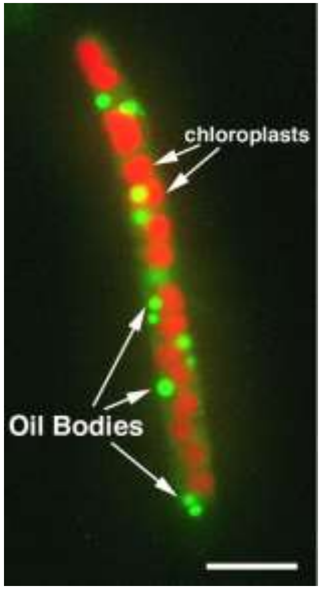
Subcontractors: Clarkson University, Center of Excellence for Hazardous Materials Management, Iowa State University, North Carolina State University, University of Pennsylvania, University of Texas

Six Integrated Teams
working towards
A Sustainable Biofuels Process

Algal Biology Team Objective:

Increase overall productivity of algal biomass and lipid/hydrocarbon content

- **Systems biology studies**
  - Genomics, transcriptomics and proteomics in carefully controlled photobioreactors (PBRs)…enabling research
  - Identify genes involved in faster growth, nutrient triggers, higher lipid/hydrocarbon productivity, lipid packaging, and lipid secretion
  - Demonstrate the utility of these genes
- **Mining natural diversity**
  - Isolate novel strains (over 600 to date)
  - Screen for lipid productivity
  - High throughput selection (FACS) of high lipid producing strains
- **Crop protection**
  - Adaptive evolution of an algal species to select for robustness
  - Genetic modification to protect the ***algal crop*** species from the environment…and vice versa
- **Culture optimization**
  - Define the minimum amount of nutrients required
  - Optimize growth conditions for strains of interest… bridge to ***Algal Cultivation Team***



NAABB Algal Biology Task at PNNL

- Ellen Panisko & Mary Lipton
- Systems Biology tasks feed the PNNL proteomics pipeline
- PNNL is applying high throughput LC-MS based proteomics to compare physiological states for protein (gene) discovery and analysis
  - Strains from four algal genera to be studied: Nannochloropsis, Chlorella, Chlamydomonas, Botryococcus
  - Seek understanding of genes:
    - controlling high growth
    - mechanisms of lipid accumulation
    - uncoupling of nutrient deprivation from lipid (triglyceride) formation
    - directing C flux to alternative (“unproductive”) storage compounds
    - hydrocarbon (isoprenoid) production

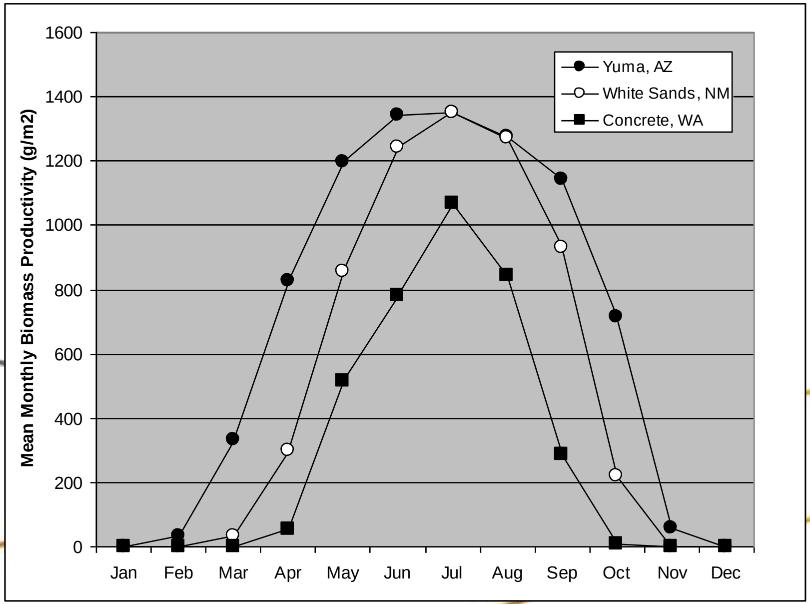
Algal Cultivation Strategies

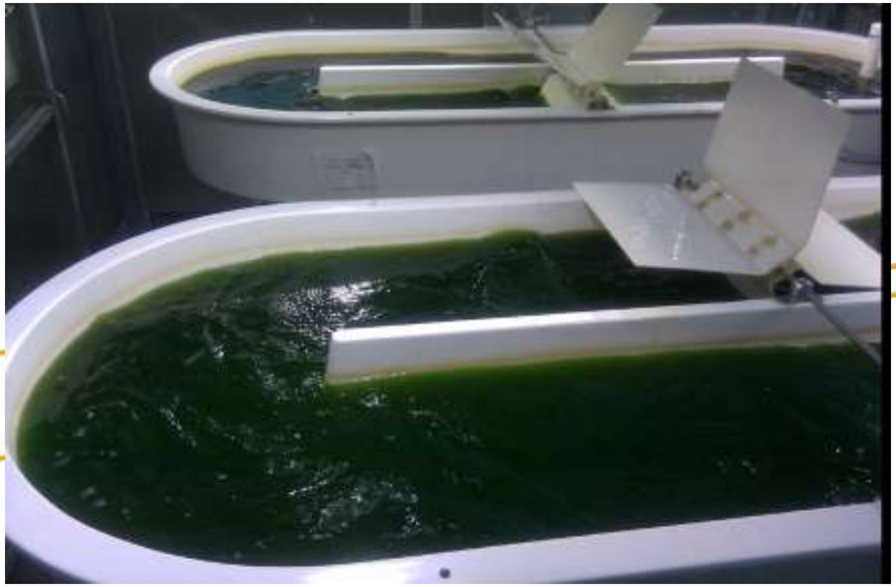
- **Increase overall productivity by optimizing sustainable cultivation and production systems**
  - Optimization of photobioreactors
  - Optimization of ponds (raceways)
  - Demonstration test beds
  - Provision of LEA and algal oil to other teams

NAABB Algal Cultivation Task at PNNL

- Provide Test Beds to NAABB
- Controlled Environment Ponds & Modeling
  - Michael Huesemann, PNNL, Marine Science Laboratory, Sequim, WA
  - Lab PBRs (1 L) and raceway ponds (1000 L) controlled for T and light
  - Access to filtered seawater and freshwater

  - Model day length and temperature effects on growth, lipid productivity, etc.
  - Develop the climatological model…test and refine it with experimental data

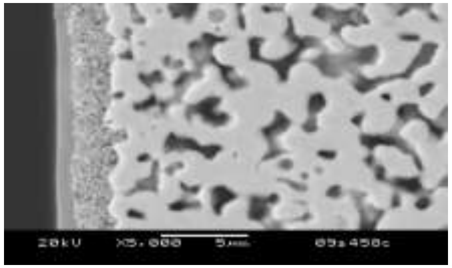




Algal Harvesting and Extraction Objectives:

Develop economical and energy efficient harvesting & extraction technologies

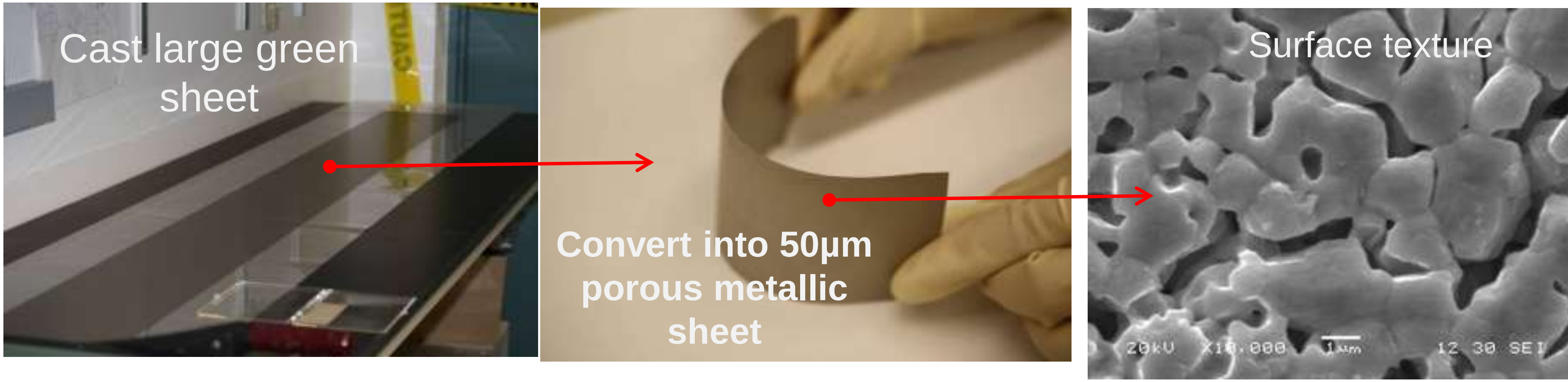
- **Harvesting technologies**
  - Acoustic focusing
  - Hybrid capacitive deionization/electro deionization (CDI/EDI)
  - Advanced membrane technology for filtration
- **Extraction Technologies**
  - Acoustic technologies
  - Mesoporous nanomaterials
  - Amphiphilic solvents



NAABB Harvesting Task at PNNL

Thin, porous metal sheet-based membranes

Wei Liu

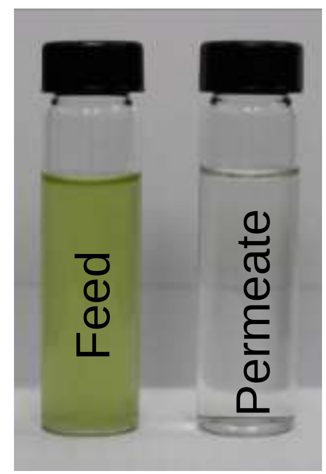


Expected advantages of new membranes:

- High surface area packing density
- Resistance to bio-fouling
- Resistance to oil and hydrocarbons
- Very high flux
- Durability

Very flexible so they can be configured as:

- Tubular
- Hollow fiber
- Spiral
- Plate & frame



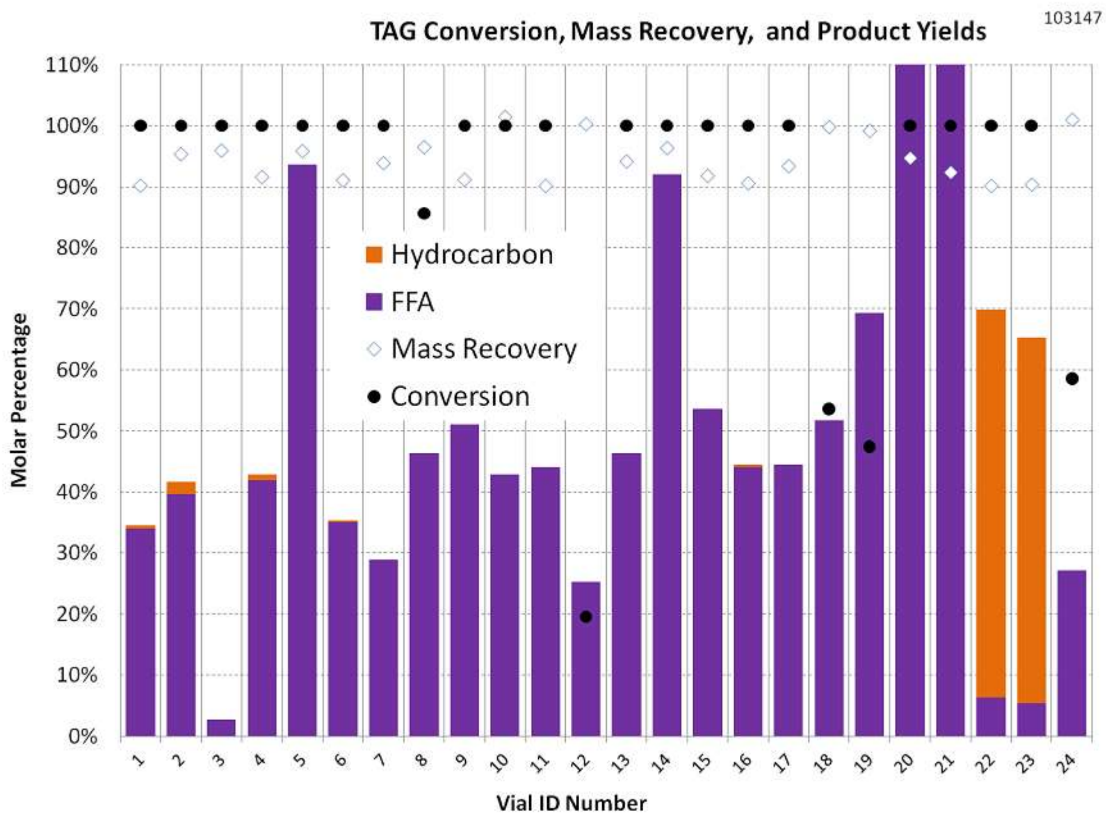
Conversion Strategies:

Develop technologies to convert lipids & algal biomass into useful fuels

- **Fuel characterization**
  - Physical and chemical properties of biofuels: fatty acid esters and hydrocarbons
  - Thermophysical and transport properties of biofuels
- **Lipid conversion to fuels**
  - Catalytic decarboxylation and deoxygenation
  - Catalytic and supercritical transesterification
- **Algal biomass conversion to fuels**
  - Catalytic gasification
  - Thermochemical gasification and power generation
  - Fast pyrolysis and hydroprocessing
  - Anaerobic fermentations to ethanol and higher alcohols/acids

NAABB Conversion Task at PNNL

- Catalytic Processing & Conversion of Algal Oil
  - Rich Hallen
  - Catalyst discovery, refinement and process demonstration for conversion of TG's to alkanes/alkenes



Valuable Co-products

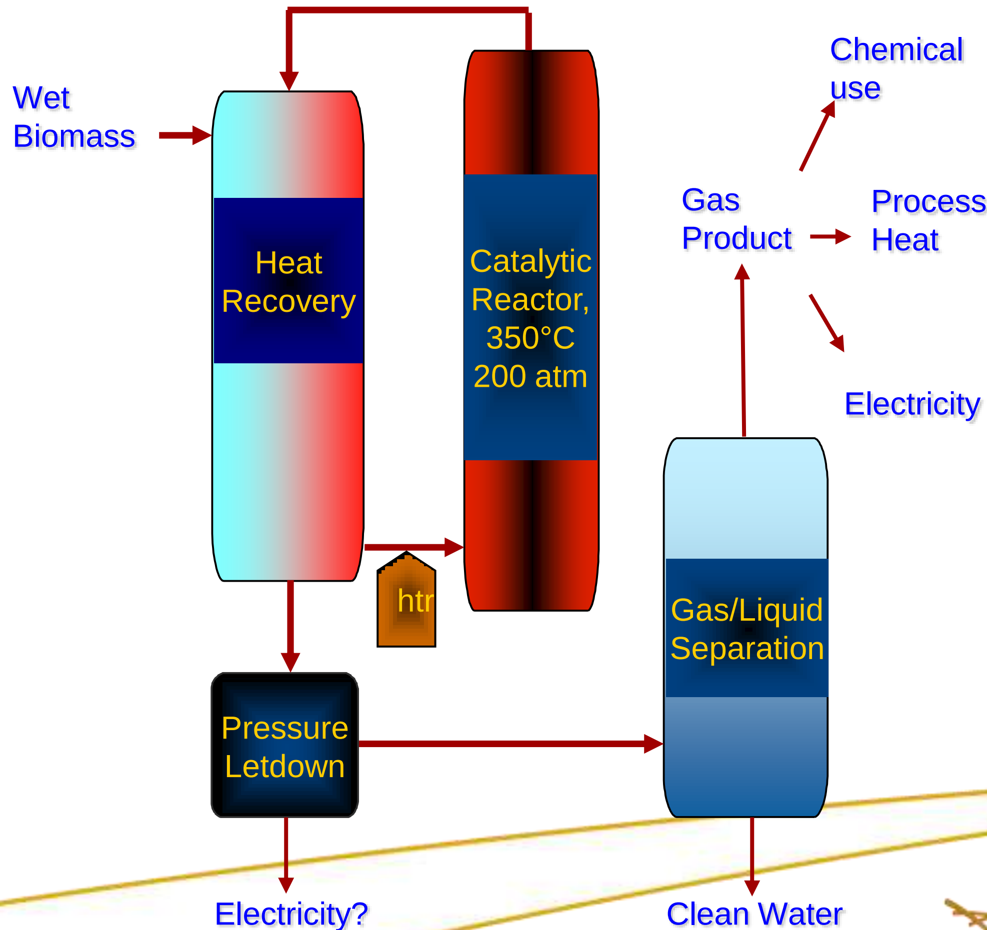
- **Develop various valuable co-products to add profitability and provide flexibility to allow responsiveness to changing demands/opportunities in the market**
  - **Livestock and mariculture feed**
    - Testing nutritional content of lipid extracted algae, LEA
    - Animal and mariculture studies
    - FDA certification of feeds
  - **Industrial Co-products**
    - Synthetic natural gas (Syngas) and thermal energy production from LEA
    - Bioplastics from proteins and lipids
    - Feedstock for nitrogen chemical industry and amino acids from LEA

NAABB Co-products Task at PNNL
Catalytic Hydrothermal Gasification

- Doug Elliott
- Low-temperature, single-step synthetic natural gas from algae or LEA
- LEA is mostly carbohydrates, protein and ash
- Metal catalyst
- High-pressure steam reforming & methanation

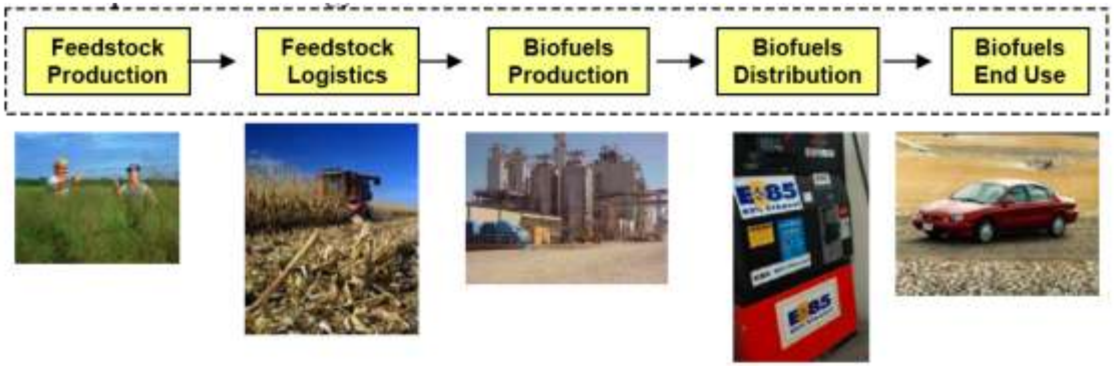
$$C_xH_yO_z + nH_2O \rightarrow aCH_4 + bCO_2$$

Equilibrium Control of Gasification



Sustainability Objectives:

- **Quantitatively assess the energy, environmental and economic viability and sustainability of the NAABB approaches to guide our strategy**
  - **Economic analysis**
    - Economic models
    - Global analysis
    - LCA and Process Analysis
  - **Resource Management**
    - Land
    - Water
    - CO_2
    - Other nutrients



NAABB Sustainability Task at PNNL

Rick Skaggs & Mark Wigmosta

Biomass Assessment Tool:

Resource Availability Assessment for Algal Biofuel Production

- Develop fine scale spatial (30 m) and temporal (hourly) information on critical resource demands and constraints
  - using best available data
  - multi-scale, physics based modeling

- Initial focus on sustainability of open systems
  - **Complete:**
    - environmental constraints
    - consumptive water use requirements
  - **Future:**
    - competition for land, water, and nutrient use
    - opportunity for co-location with sources of CO_2 and nutrients

Resource Constraints on Large Scale Sustainable Microalgae Biofuel Production

Land

- 1200 acres of contiguous flat land (slope <= 1 %) = “farm scale”
- exclude cropland, urban, protected, sensitive areas

Climate

- solar radiation and duration
- pond water temperature : 15 – 35 C^{o}
- diurnal variation

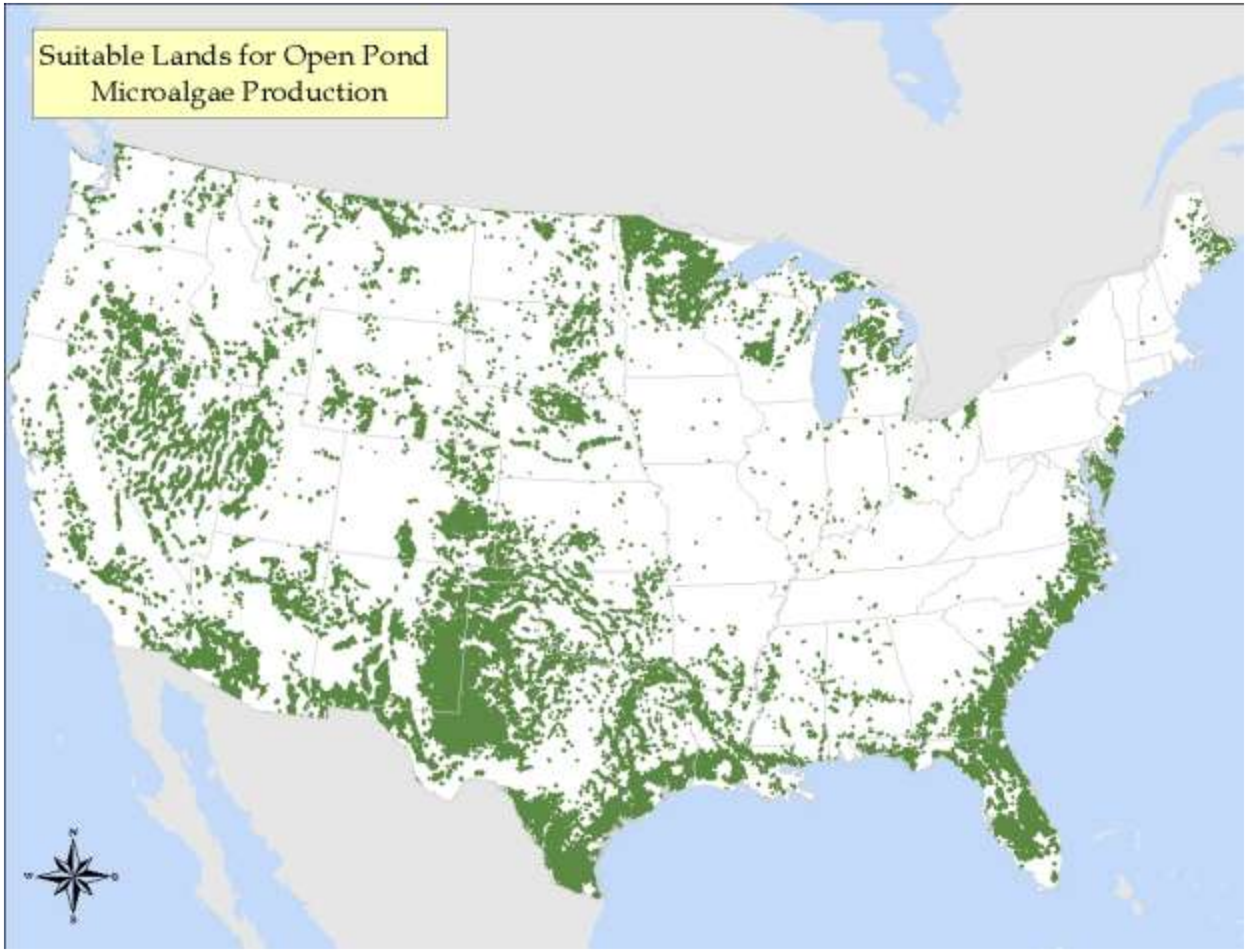
Water Supply

- avoid competition with food production
- saline groundwater, seawater, other brackish water
- quantify water use

Carbon Dioxide & Nutrients

- transportation cost
- co-location with power plants, refineries, wastewater treatments plants, etc.

Land Constraints: Suitable Land (30-m Grid)



Slope ≤ 1 %

Exclude:
- Croplands
- Urban
- Open water
- Wetlands
- Riparian zones
- State Parks
- NPS protected
- FS protected
- Wilderness
- FWS protected
- BLM protected
- Military

5.5% of conterminous U.S. land area

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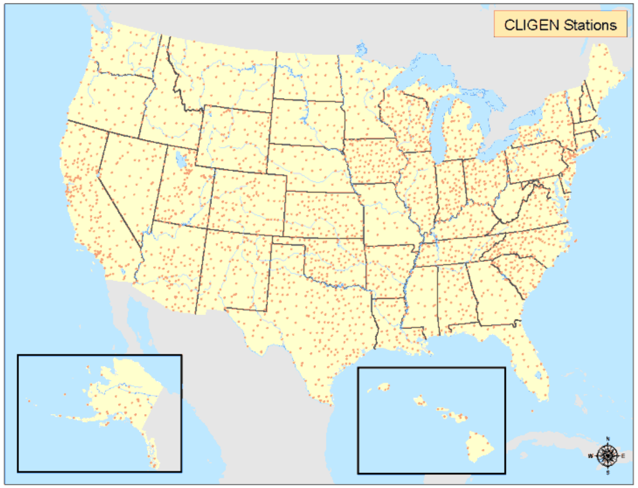
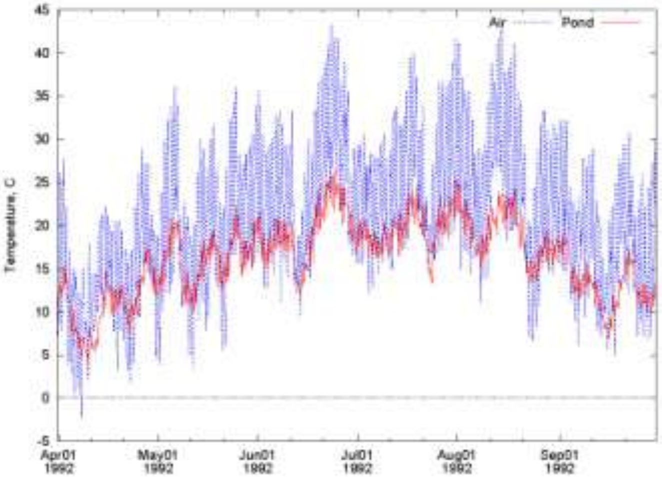
Climate Constraints: Unit Farm Water-Energy Balance and Growth Models





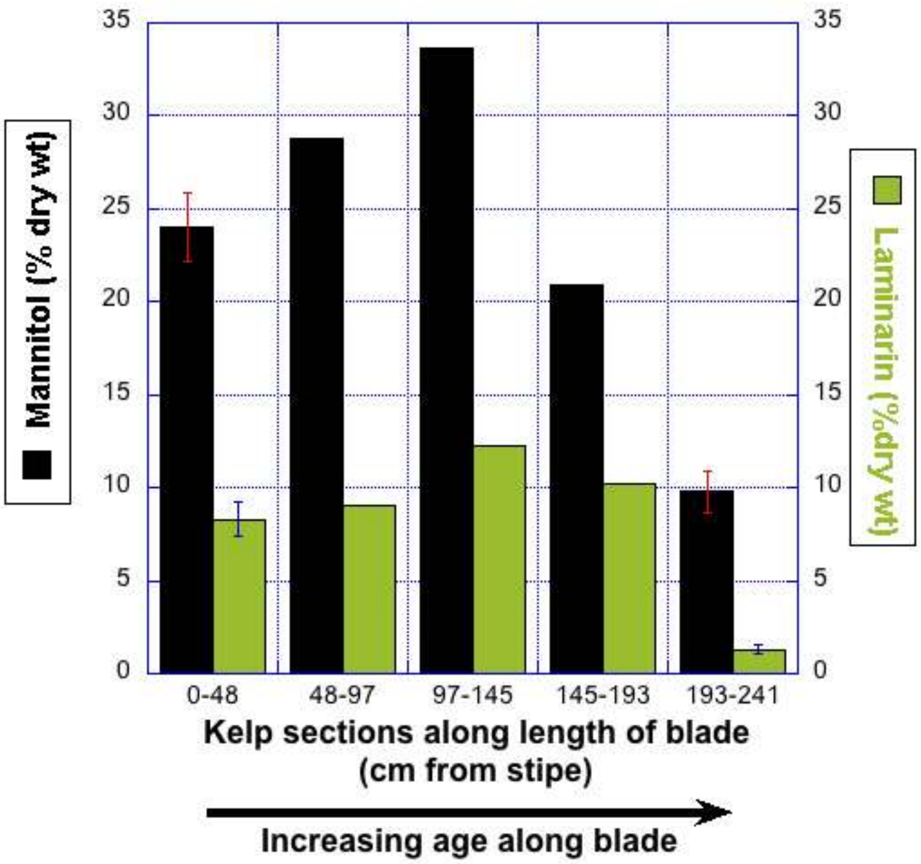
- 30 years of *hourly* meteorology for ~2600 locations
  - disaggregate CLIGEN daily to hourly and map (via PRISM) to unit farm
  - air temperature, wind speed, solar radiation, humidity, etc
- Two-dimensional Hydrodynamic Pond Model
  - water temperature, evaporative loss
- **Pond Growth Model** ***Connectivity to Algal Cultivation Task***
  - hourly to annual biomass production output

Canada-USA; NRC-PNNL Project on Macroalgae

Potential coastal biorefinery feedstock
Carbohydrate rich (not high lipid)

1. **Compositional characterization** of a species of kelp, *Saccharina latissima*, common to the east coast (Canadian Atlantic) and west coast (US Pacific) to be conducted on samples across a one year growing season
2. **Thermochemical conversion** of kelp biomass to fuel molecules by hydrothermal liquefaction
3. **Biochemical conversion**: isolation and screening of fungi for conversion of macroalgal biomass to: sugars, fuel molecules, enzymes, and co-products

Carbohydrate composition along blade of *Saccharina latissima*



Hydrothermal Liquefaction of Macroalgae

- **HTL Process**
  - Prepare biomass slurry in water
  - T > 300°C
  - P ~ 200 atm
  - Residence time = minutes
  - Reducing gas (optional)
  - Catalyst (optional)
  - Biooil output

- **Macroalgal biomass challenges**
  - Viscosity of polysaccharides
  - High ash content of unusual composition

Biochemical Conversion of Macroalgal Biomass

- Isolation of heterotrophs, fungi and bacteria, from decaying seaweed
- Screen promising fungal/bacterial isolates for production of: fuels or fuel precursors, sugars, other chemicals and enzymes

Acknowledgments

- **John Holladay**, NAABB leadership, business development
- **Dan Anderson**, NAABB leadership, and industry experience
- **Blaine Metting**, FCSD algal biology, and industry experience
- **Ellen Panisko**, NAABB proteomics
- **Mary Lipton**, NAABB proteomics
- **Michael Huesemann**, NAABB cultivation
- **Wei Liu**, NAABB harvesting
- **Doug Elliott**, NAABB & macroalgae thermochemical conversion and catalysis
- **Rich Hallen**, NAABB thermochemical conversion and catalysis
- **Mark Wigmosta**, NAABB resource assessment
- **Rick Skaggs**, NAABB resource assessment
- **Guri Roesijadi**, macroalgae expertise and market assessment
- **Stephen O'Leary**, NRC, Canada, macroalgae expertise

Thank-you!