# An Algal Biofuels Consortium


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*and*

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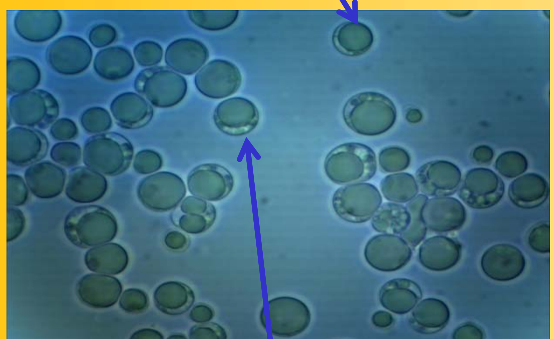
*Pacific Northwest National Laboratory*


*DOE-EERE Technical Advisory Committee*
*Dec.15, 2010*

Work Funded By USDOE Office of Biomass Program, DE-EE0003046

# Biofuels from Algae

4-50%
Lipid biomass



50-90%
Other biomass

**Rapid growth rate**

Double in 6-12 hours

**High oil content**

4-50% non-polar lipids

**All biomass harvested**

100%

**Continuous harvesting**

24/7, not seasonally

**Sustainable**

Capture up to 90% of injected $CO_2$

Utilize waste water

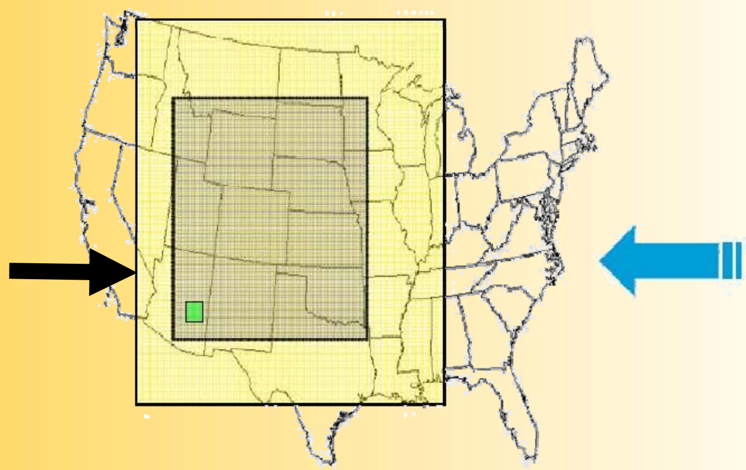
Non-food

# The Promise of Algae-Based Biofuels

**Algae has potential advantages over corn, cellulosic materials, and other crops as an alternative to petroleum-based fuels**

Figure courtesy of Sandia National Laboratory

| Crop | Gallons of Oil per Acre per Year |
|---|---|
| Corn | 18 |
| Soybeans | 48 |
| Safflower | 83 |
| Sunflower | 102 |
| Rapeseed | 127 |
| Oil Palm | 635 |
| Micro Algae | 1000 - 7000 |



The amount of land required to replace 50% of the current petroleum diesel usage using corn, soybean, and algae.

- *High biomass productivity potential*
- *Oil feedstock for higher energy-content fuels*
- *Can avoid competition with agricultural lands and water for food & feed production*
- *Can use non-fresh water, resulting in reduced pressure on limited fresh water resources*
- *Captures CO2 and recycles carbon for fuels and co-products*

Land Needed for Biofuel to Replace 50% of Current Petroleum Diesel using oil from:
Corn
Soybean
Algae

# NAABB Objectives

## Process Economics

- Operating cost
  - $0.40/gal processing cost (oil)
  - <$1/gal processing cost (LEA)
- Capital Cost (Industry benchmarks for oil)
  - $1/annual gallon installed capacity (biodiesel)
  - $2/annual gallon installed capacity (green diesel)

## Sustainability

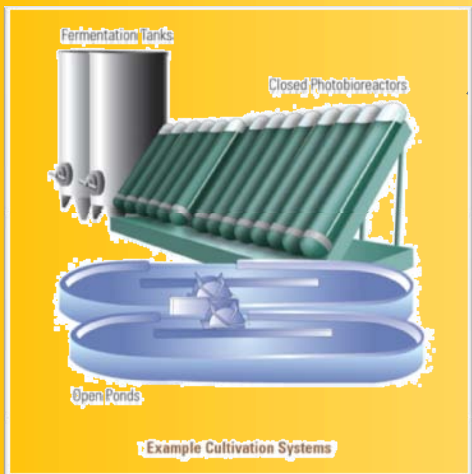
- Reduced $CO_2$ Emissions
- Water usage: less than 0.75 gal $H_2O$ / gal fuel
  - (differentiate between consumptive and process water)
- Nutrient recycle
  - Oil conversion: N/A
  - LEA: 90% recycle nutrients

## Energy Return on Investment (>> 1)

- Energy required for conversion is 10% or less of energy in fuel

# Technical Challenges

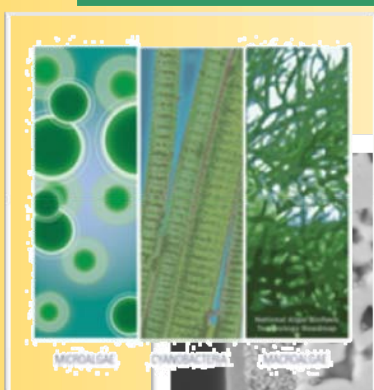
## Biology and Cultivation

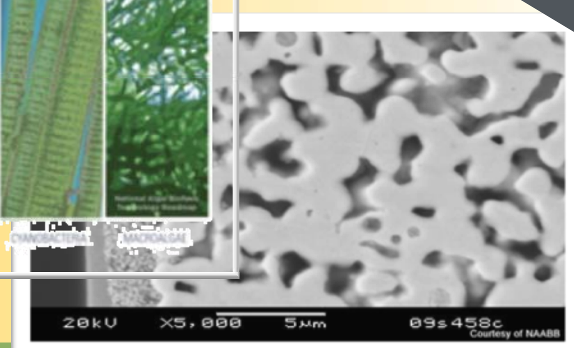



- Cultivation system design
  - •Temperature control
  - •Invasion and fouling
- Cultures
  - • Growth, stability, and resilience
- Input requirements
  - •$CO_2$, $H_2O$ sources, energy
  - •Nitrogen and phosphorous
- Siting and resources

- Energy efficient harvesting and dewatering systems
- Biomass extraction and fractionation
- Product purification

## Biomass Harvesting and Recovery






A nano-membrane filter being developed by a NAABB partner.

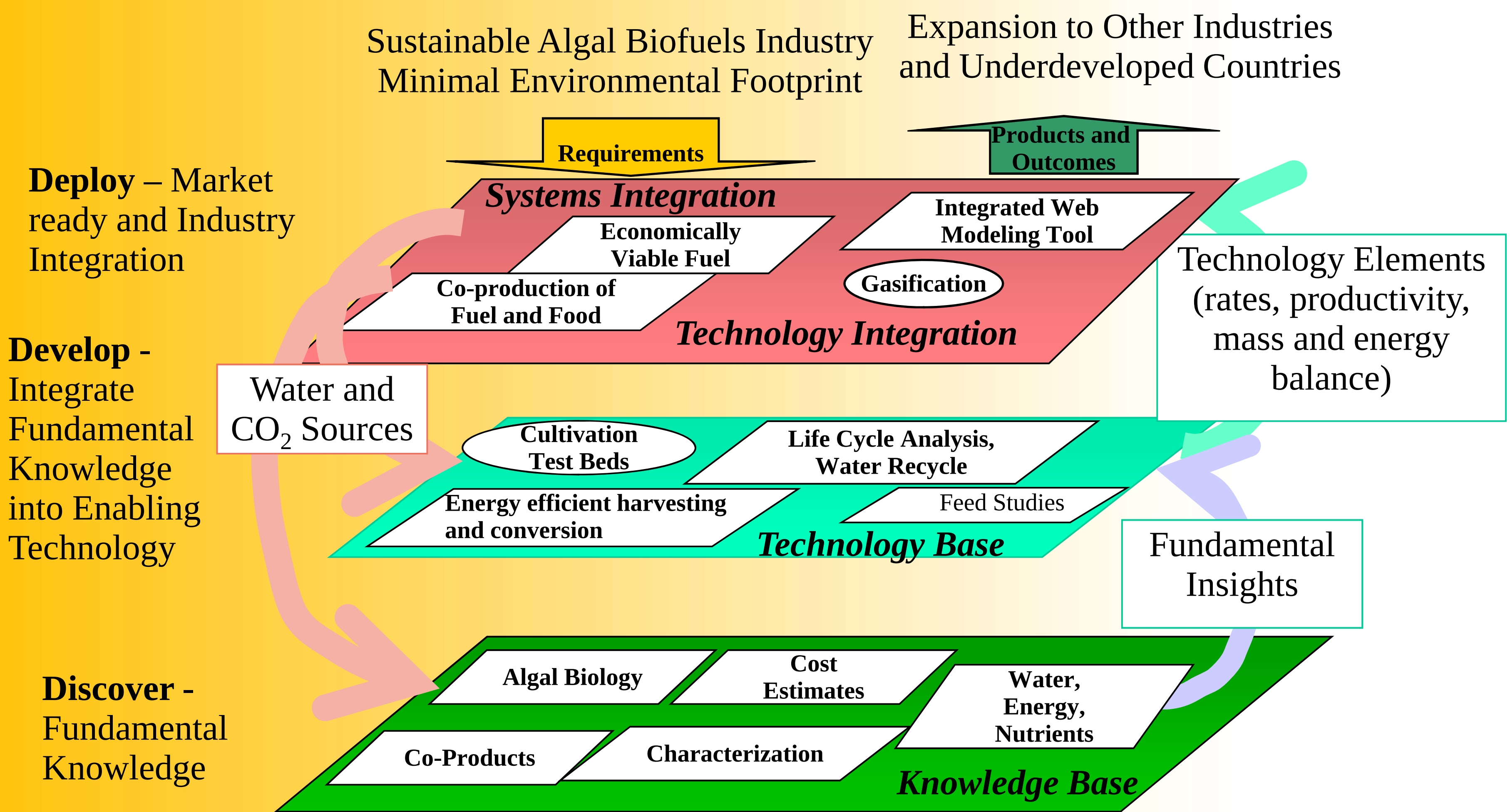
A gasifier being used by a NAABB partner to convert algal biomass to fuels

- Process optimization
  - •Thermochemical
  - •Biochemical
- Fuels characteristics
- Co-Products

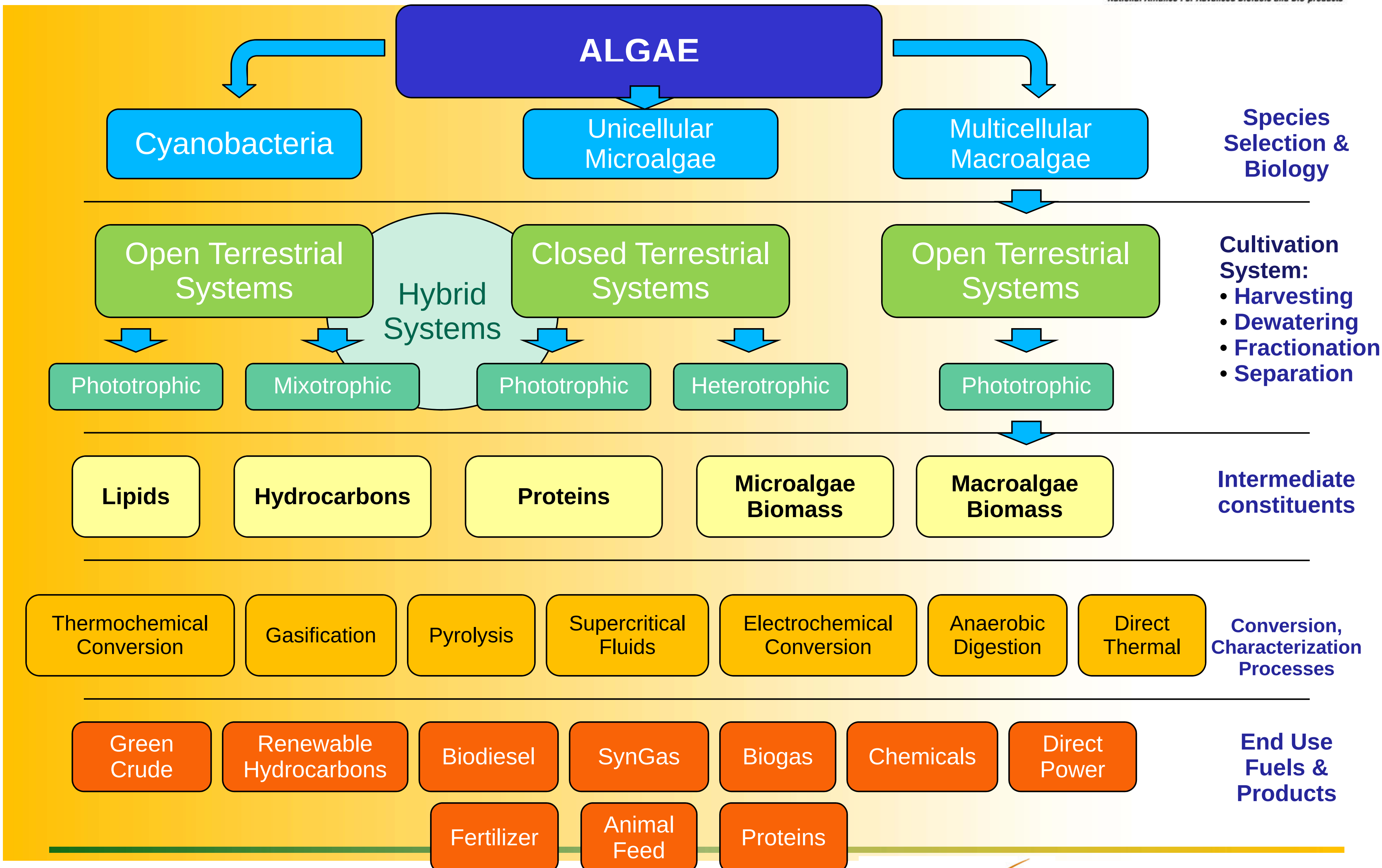
## Conversion and End-use

# NAABB Vision

## Catalyzing a Sustainable Energy-Optimizing Algal Industry



# NAABB R&D AND DEPLOYMENT PROGRAM

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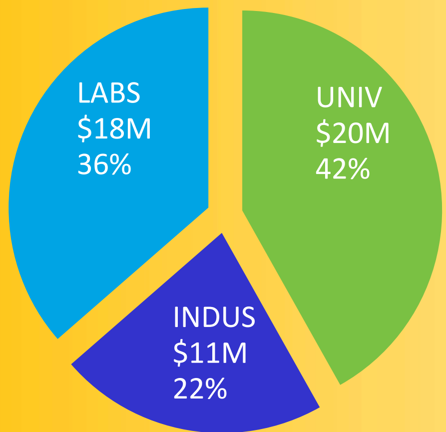
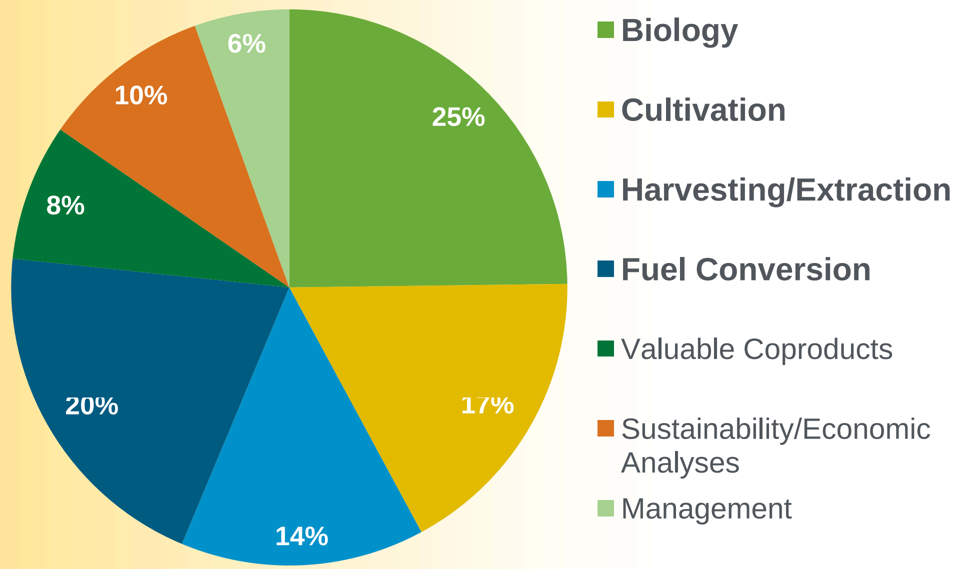
# NAABB DOE Resource Allocation FY10-FY13




(By Partners, DOE Share Only)

- ARRA funded algae R&D consortium
- Led by Donald Danforth Plant Science Center (DDPSC)
  - Los Alamos National Lab
  - Pacific Northwest National Lab
- Activities in 14 states

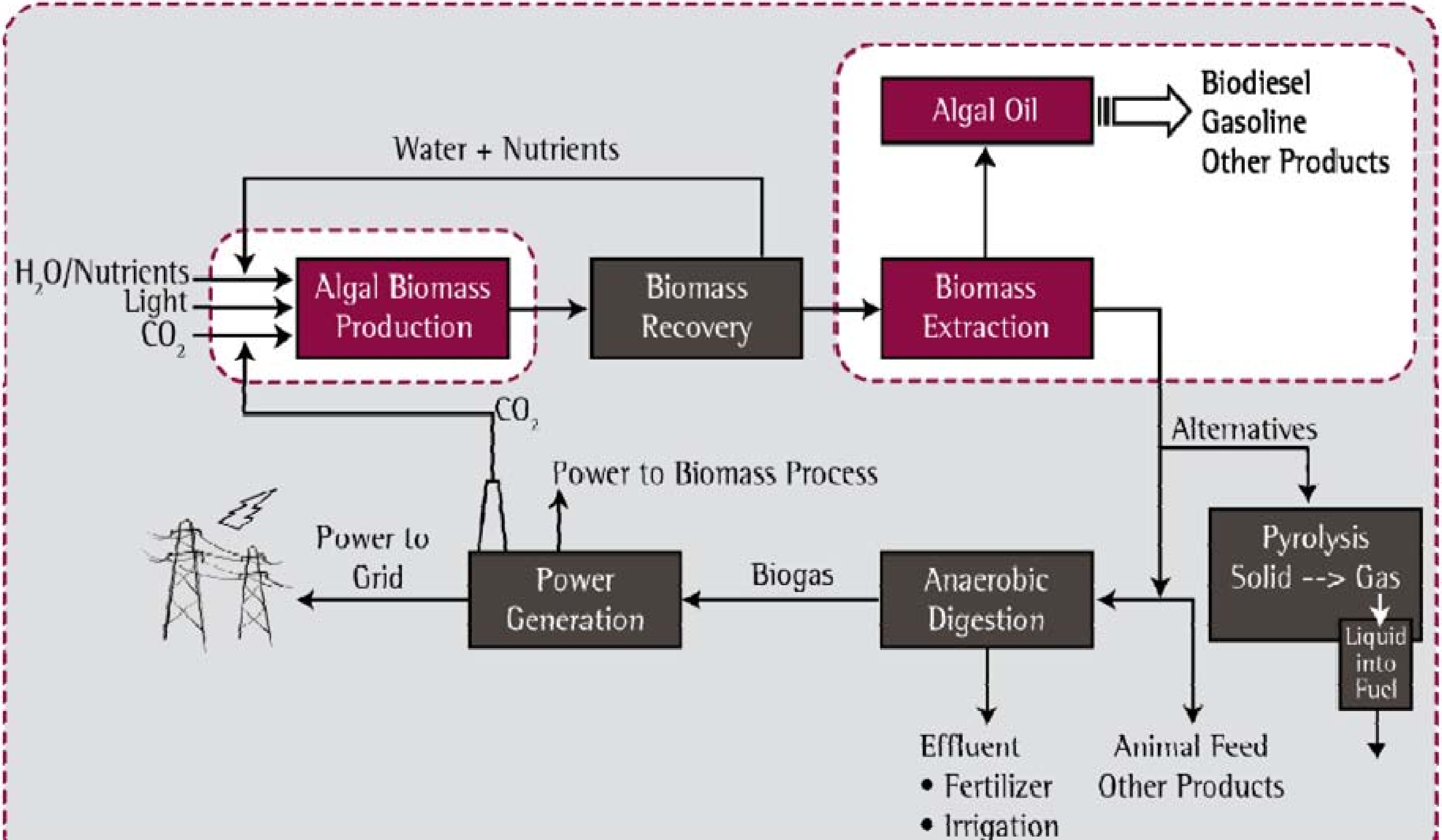
**Secretary Chu Visits DDPSC**
(left to right: R. Sayre, W. Danforth, S. Chu)




(By Task, DOE and recipient cost share)

# NAABB Partners Contributions

# NAABB Process Flow

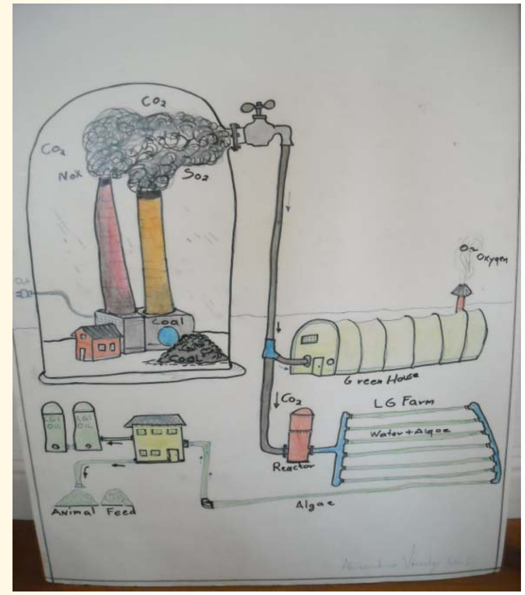



S. Deng, NMSU, 2010 (on behalf of NAABB)

# NAABB Specific Objectives

National Alliance For Advanced Biofuels and Bio-products

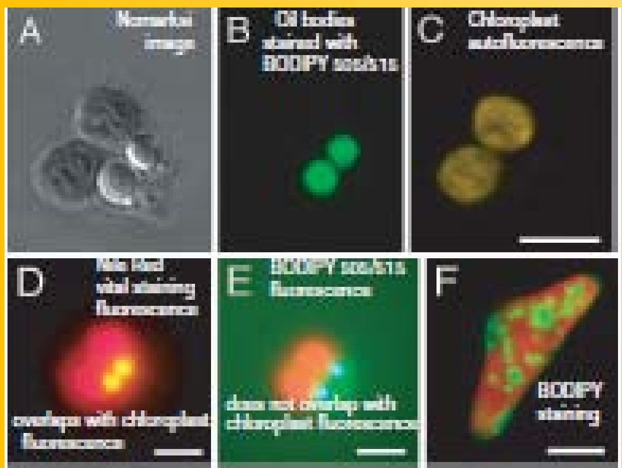
- **Developing technologies for cost-effective production of algal biomass and lipids**
  - **Algal Biology -** Increase overall productivity of algal biomass accumulation and lipid/hydrocarbon content
  - **Cultivation -** Increase overall productivity by optimizing sustainable cultivation and production systems
  - **Harvesting/Extraction -** Develop cost-effective and energy efficient harvesting and lipid extraction technologies

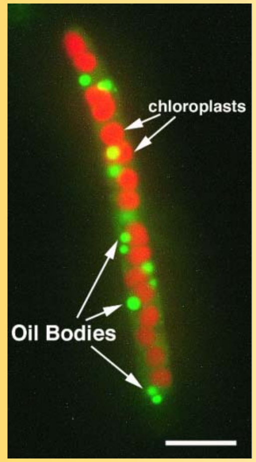



- **Developing economically viable fuels and coproducts**
  - **Fuel Conversion –** Develop technologies to convert lipids/hydrocarbons and biomass residues into useful fuels
  - **Valuable Coproducts -** Develop a set of valuable coproducts to add profitability and provide flexibility to allow responsiveness to changing demands/opportunities in the market

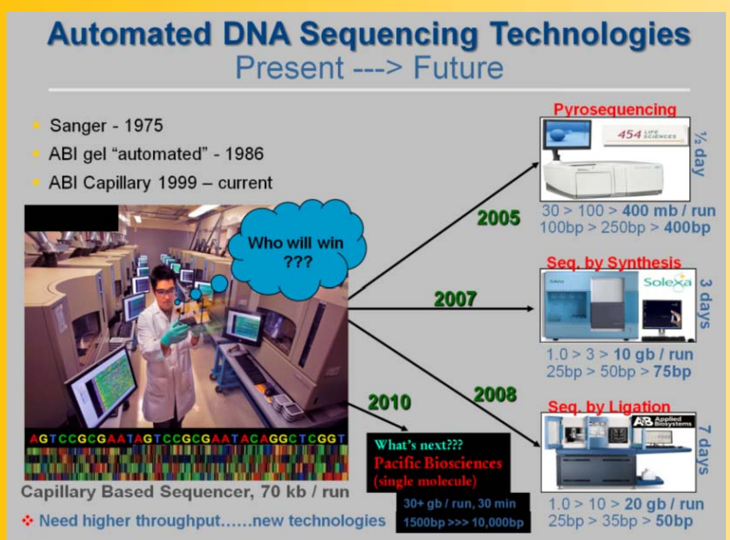
- **Providing a framework for a sustainable algal biofuels industry**
  - **Sustainability Analysis –** Quantitatively assess the energy, environment, economic viability and sustainability of the NAABB approaches to guide our strategy

# ALGAL BIOLOGY




## Phenotypic and Genotypic Analysis




**GOALS:**

- **High rate growth cultures**
- **High lipid/hydrocarbon content**
- **Crop protection**
- **New organisms from diversity of nature**

**Systems Biology**

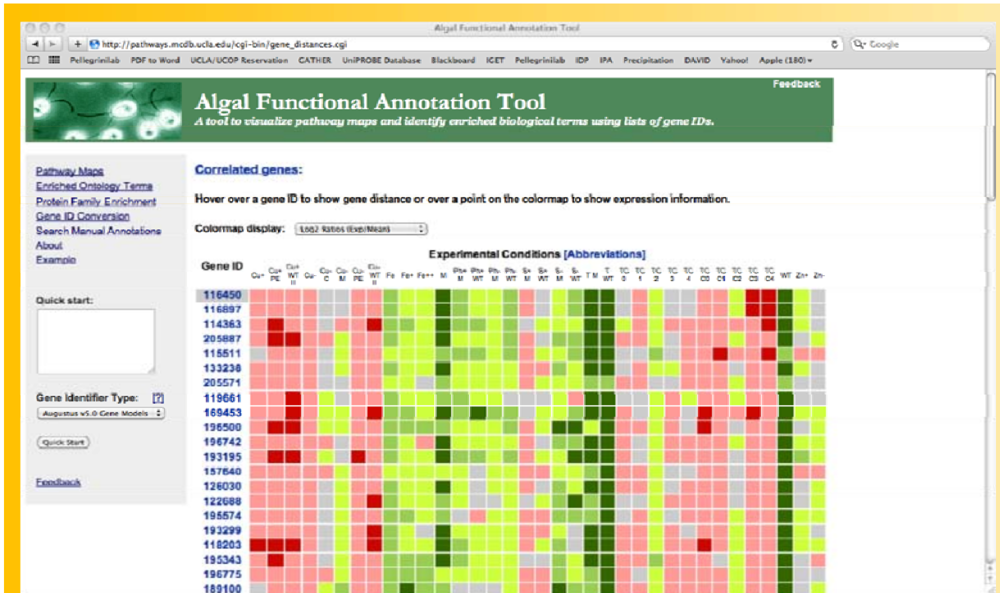
- Sequencing/Transcriptomics/Proteomics
- Mutagenesis
- Genetic modification

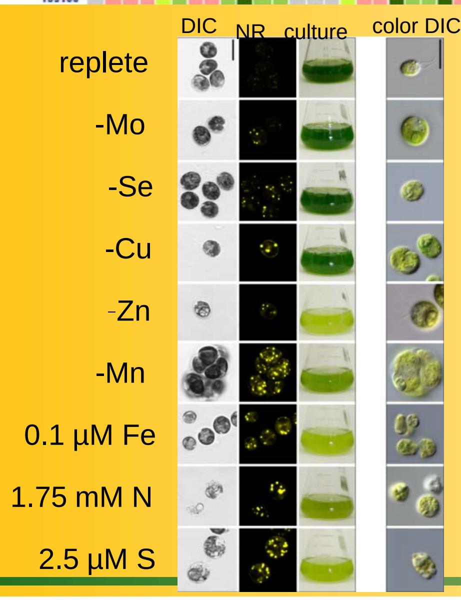
**Model & Production Organisms**:

- Chlamydomonas reinhardti
- Chlorella protothecoides
- Nannochloropsis salina
- Botryococcus braunii

# Algal Pathway Annotation Tool (Merchant, Pellegrini Labs)

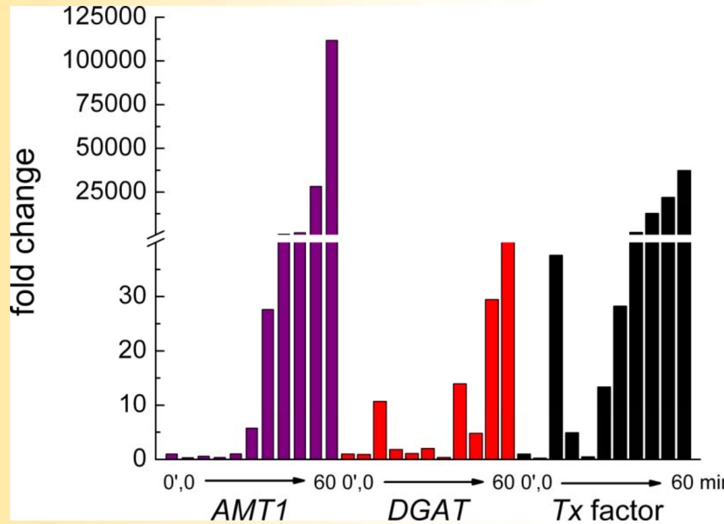
NAABB National Alliance For Advanced Biofuels and Bio-products




Facilitates the use of RNA-Seq data by

- •Input lists of IDs from differential expression analyses
- •Associates genes with known metabolic pathways
- •Annotates gene data from JGI for lists of genes
- •Finds genes whose expression correlates with gene of interest




Stress induced increase in DGAT
Tx factor increase precedes DGAT increase

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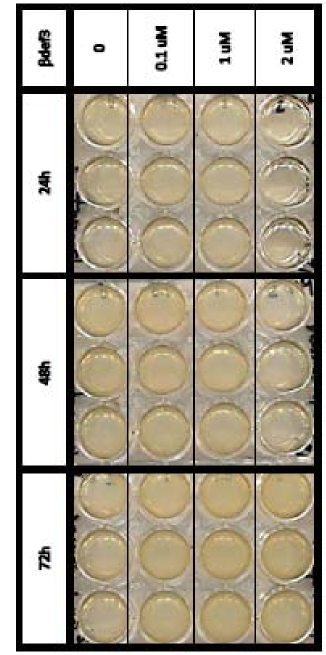
# Identification and Control of Biocontaminants

PCR and DNA Sequencing using universal primers designed for

- 16S rRNA (prokaryotes)
- 18S rRNA (eukaryotes)
- 23S cp-rRNA (algal contaminants)




Contaminants identified in algal cultures include:

gram-positive *Mycrobacterium sp.* and *Bacillus sp*,

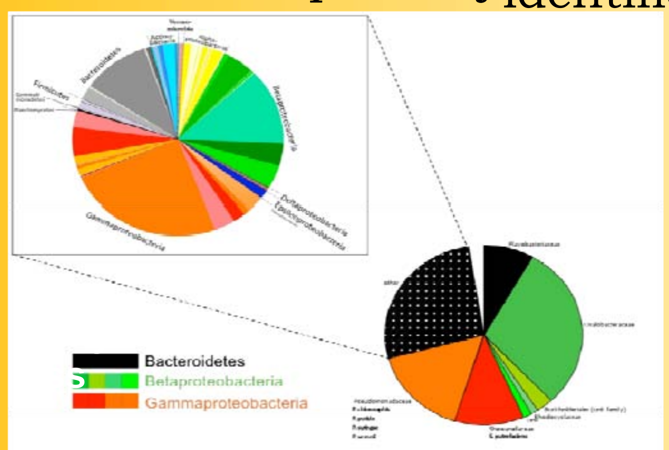
gram-negative *Stenotrophomonas maltophilia*

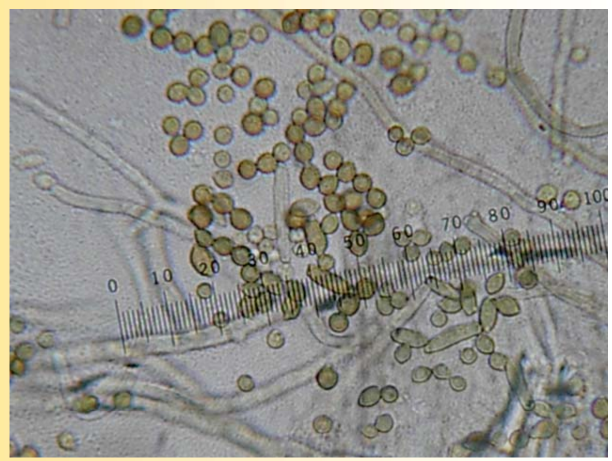
fungus *Cladosporium sp.*

Bacteriacidal peptides identified

D-amino acid control of bacterial growth demonstrated

Probiotic bacteria partially identified



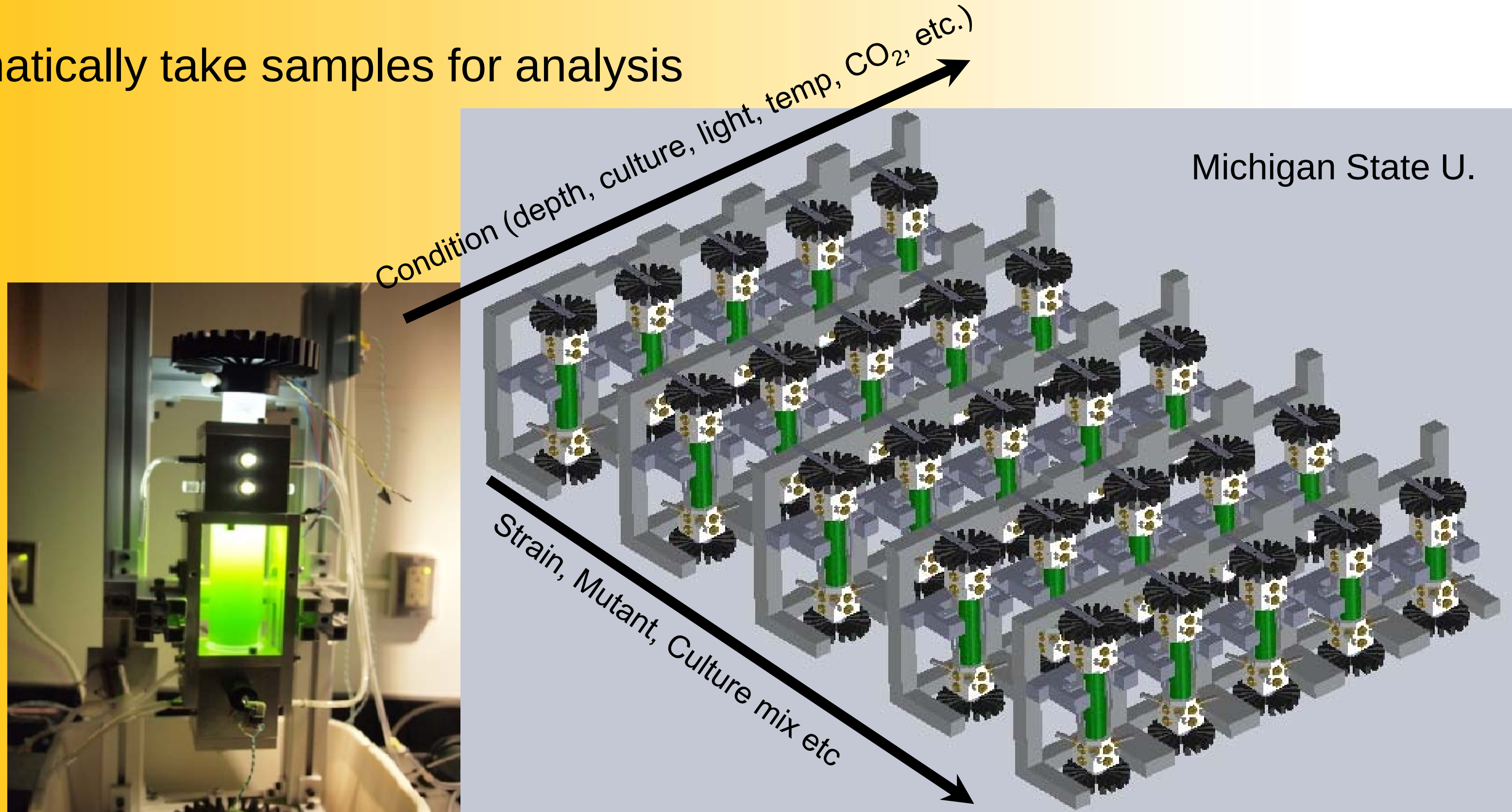



# New High Throughput Tools for Control of Cultures

Grow and maintain (stat) many strains/mutants under different conditions that **simulate real 'pond' conditions**

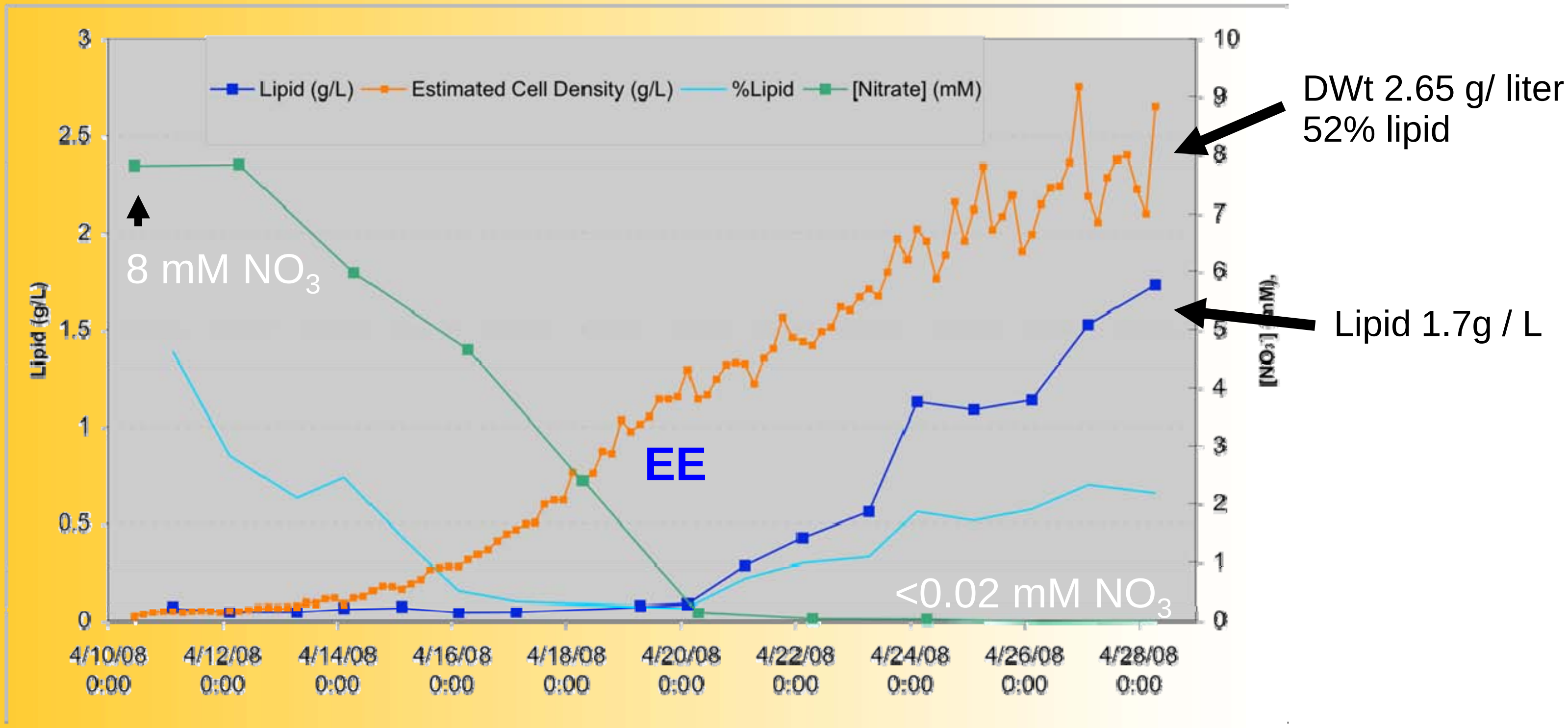
Measure growth light penetration, many photosynthetic and other properties **continuously**

Automatically take samples for analysis



# Maximizing Culture Growth Conditions

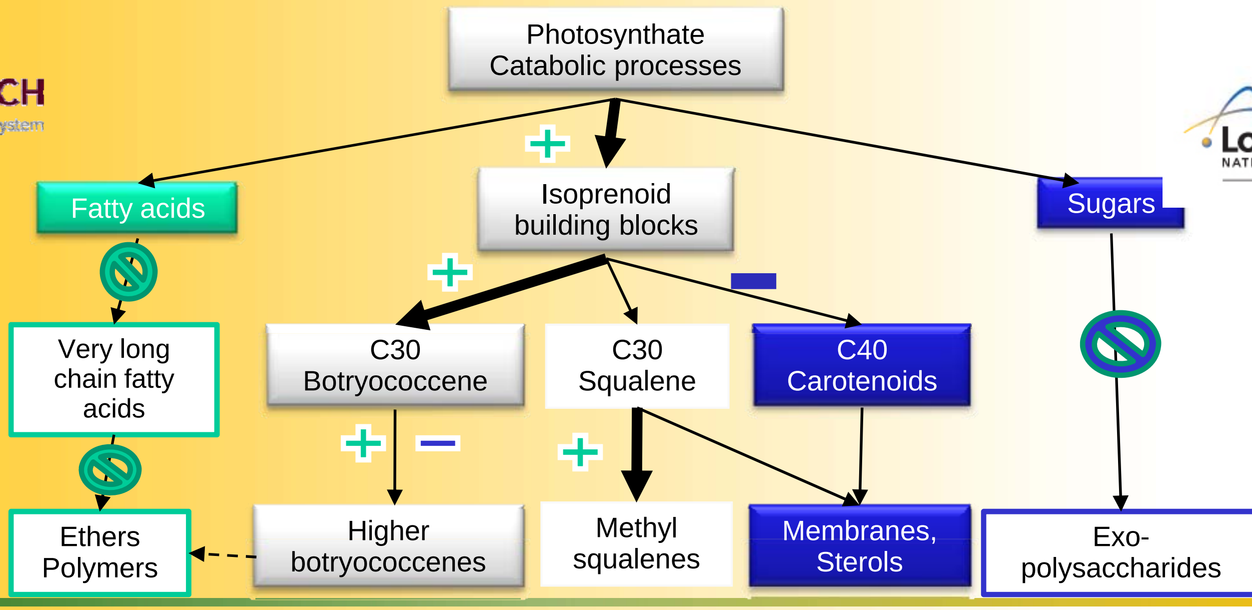
## 10X medium: growth and high lipid production simultaneously




- Lipid production starts after N is removed from media.
- Lipid production and growth occur simultaneously.
- High lipid production occurs (~50% of dry weight).
- High-lipid algae are vigorous inocula for next cycle.
- Algae quickly remove N from medium, store it and use it later.

# Algal Genetics, Selection, and Manipulation

- **Methods to genetically modify algae**
- **Plasmid vectors to transfer genetic material between species, and sustained in different algal species.**
- **Plasmid vectors to insert cloned algal genes of interest for their over-expression under the control of promoters that function well in algae.**
- **Modulate oil biosynthetic pathway enzymes to optimize hydrocarbon composition and yield for the production of carbon-neutral, renewable biofuel production.**




AgriLIFE RESEARCH Texas A&M System

The University of Arizona

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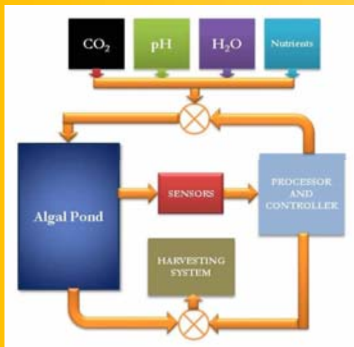
# Cultivation

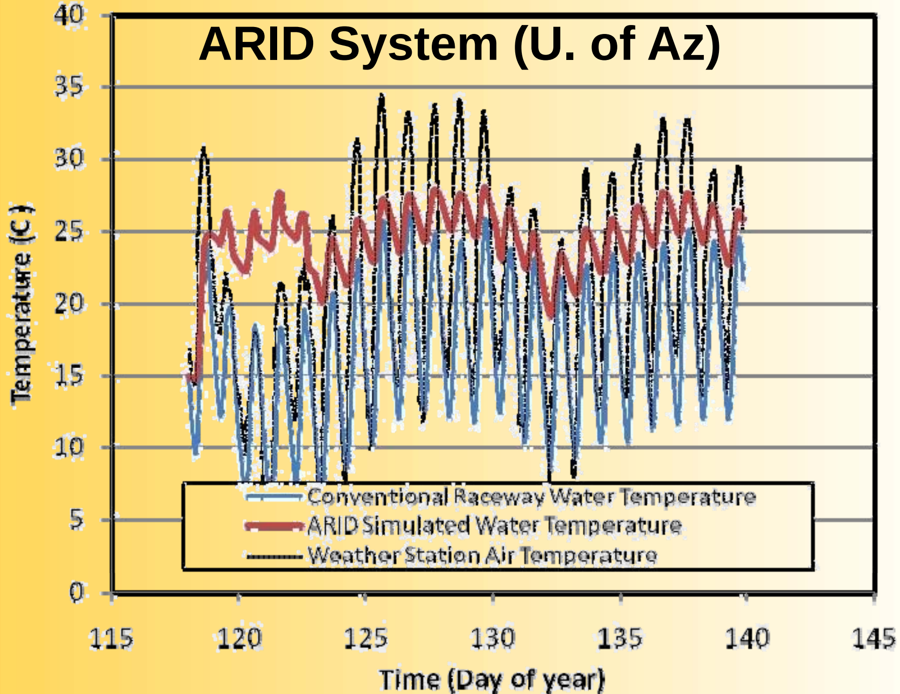


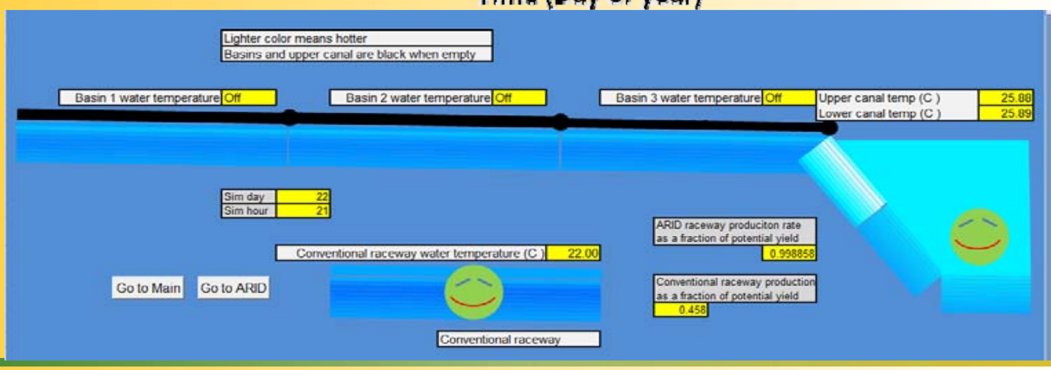
## Productivity, Environment, Nutrients, Water

**Real-time In-situ Monitoring (JA Thomasson, TAMU)**

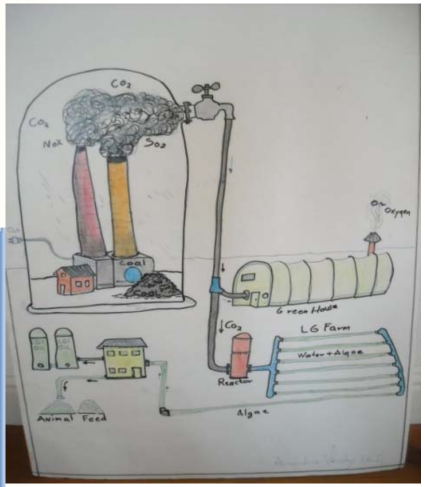



Texas A&M Pecos Site




Solix Biofuels Coyote Gulch





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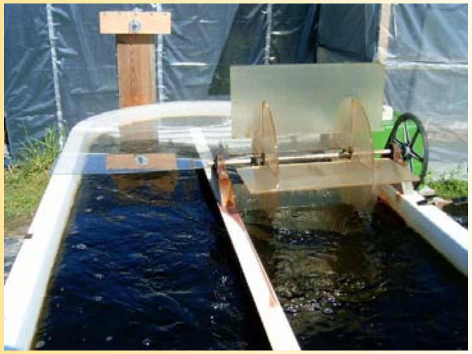
# Climate Simulated Culturing

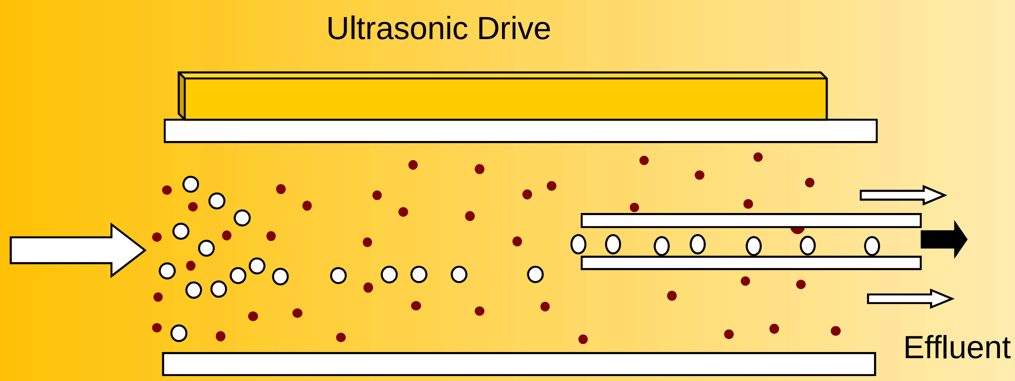
- Tiered screening: From test-tube to outdoor pond

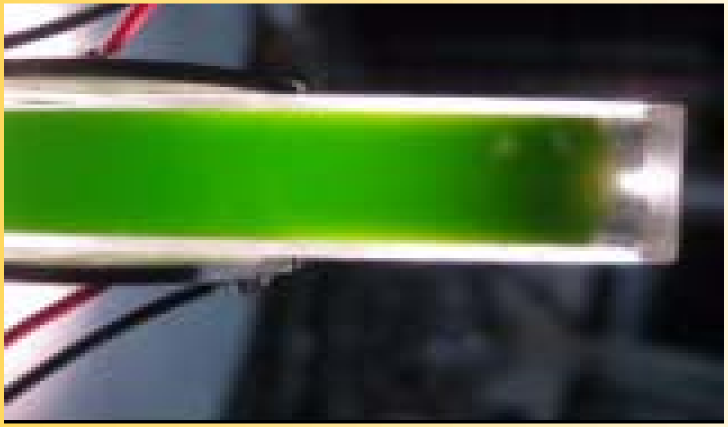
| Screening Under Optimum Culture Conditions | Climate-Simulate Culturing in Sterile Photobioreactors | Climate-Simulate Culturing in Outdoor Pilot-Scale Ponds | Mass-Culturing in Outdoor Ponds |
|---|---|---|---|
|  |  |  |  |

- Goal: Find best match between strain and geographic location (climate), with the goal of maximizing biomass and lipid productivities.

# Acoustic Concentration of Algae

## Los Alamos National Laboratory (2010 R&D 100 Winner)

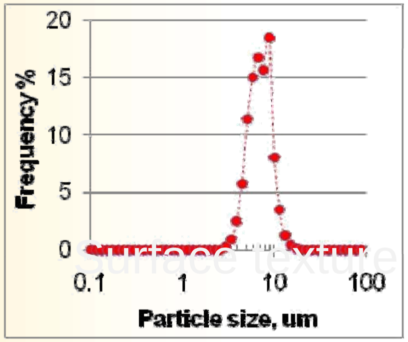


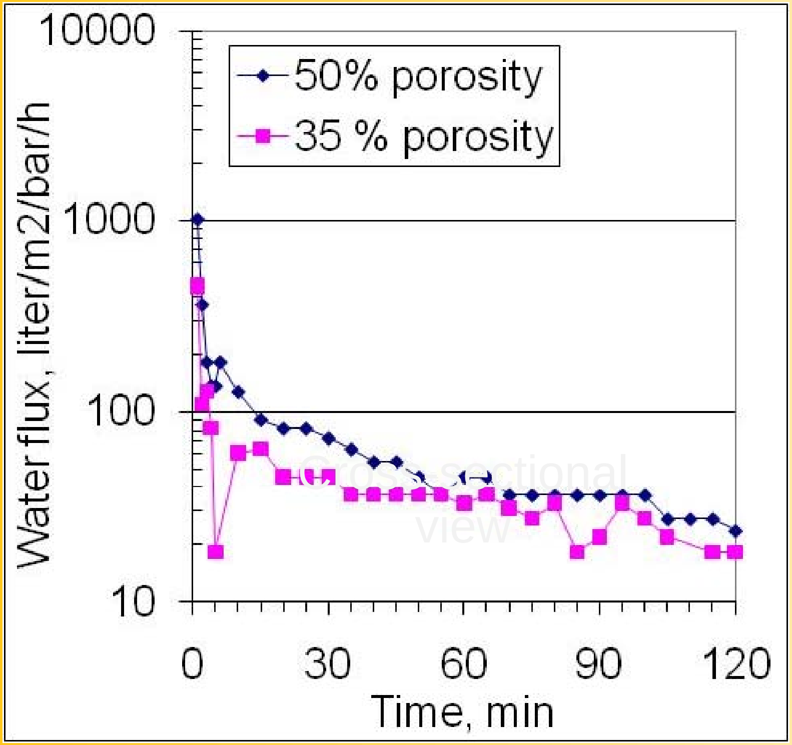



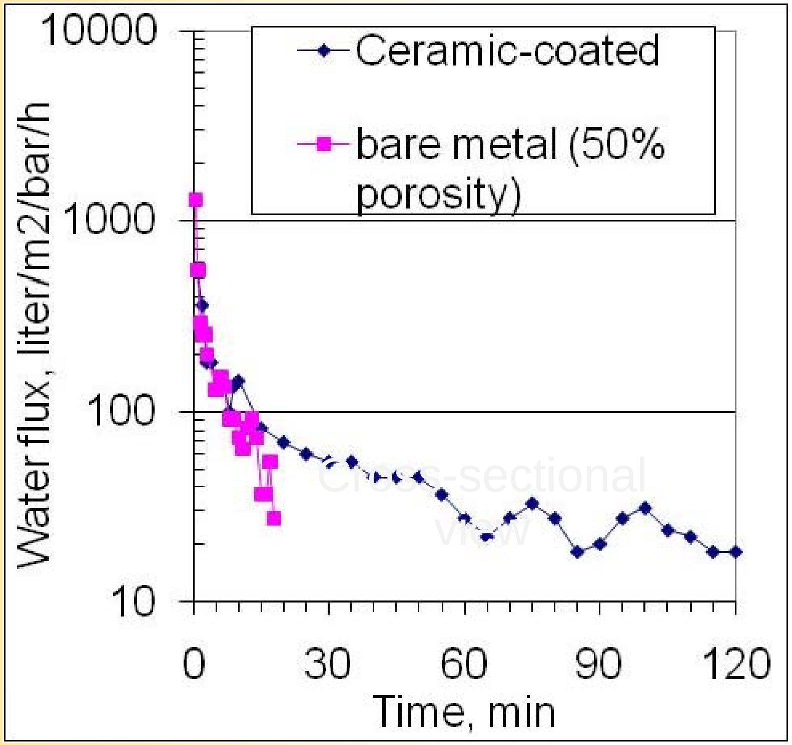
It is estimated that less than 5% of the energy content of the alhgal oil is utilized to concentrate (>25X) algae by ultrasonics

# Filtration Systems for Algae

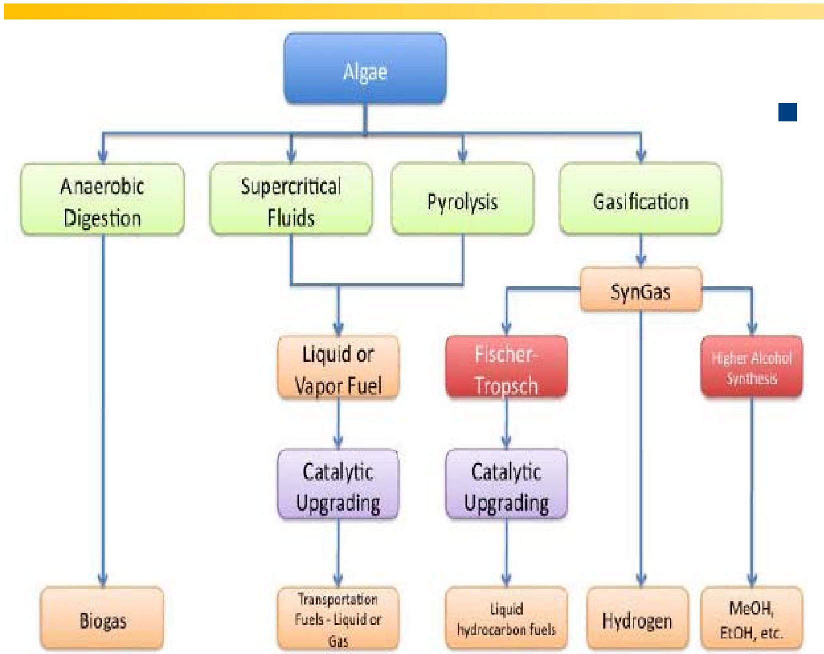
- Filtration under a constant ΔP at very low surface velocity (~0.03cm/s).
- Algae particles (2 to 20um) are easily filtered out.
- Water flux is very high at the beginning but rapidly declines with time on stream.



# Conversion Strategies




- **Development of technologies to convert lipids/hydrocarbons and biomass residues into useful fuels**
  - **Lipid conversion to fuels** • *Catalytic decarboxylation and deoxygenation* • *Catalytic and supercritical transesterification*
  - **Biomass conversion to fuels** • *Catalytic gasification* • *Thermochemical gasification and power* • *Fast pyrolysis and hydroprocessing* • *Anaerobic fermentation to EtOH and gasoline*
  - **Fuel characterization** • *Physical and chemical properties of algal esters and biofuels* • *Thermophysical and transport properties of biofuels*


Fixed Bed Catalytic Reactor (PNNL)

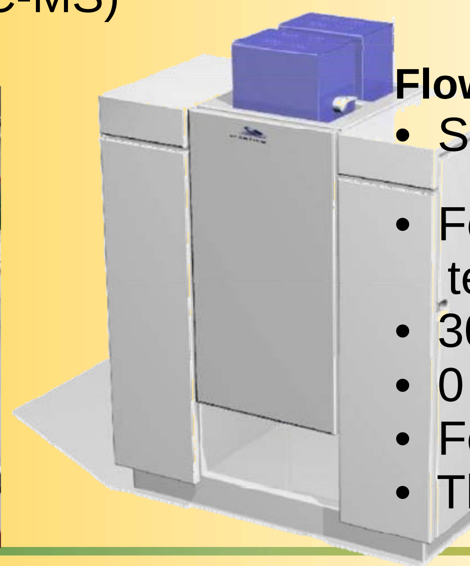

T300 Heterogeneous Catalyst (Catilin)


Fuel properties characterization CSU Engine Lab; UOP,

# Catalyst Research – Combinatorial and High Throughput Screening


**Workflow Stations**
- Weighing and solids delivery
- Liquid handling and delivery
  - Catalyst preparation and feed delivery
  - Sample prep/derivatization
- Calcine and reduction (inert gas glovebox)
- Analytical (HPLC, GC-FID, GC-MS)

**Batch Reactor**
- Pressures up to 1000 psig
- Temperatures up to 400°C
- Orbital shaking from 100 to 1000 rpm
- Computer controlled and monitored
- Safety shutdown



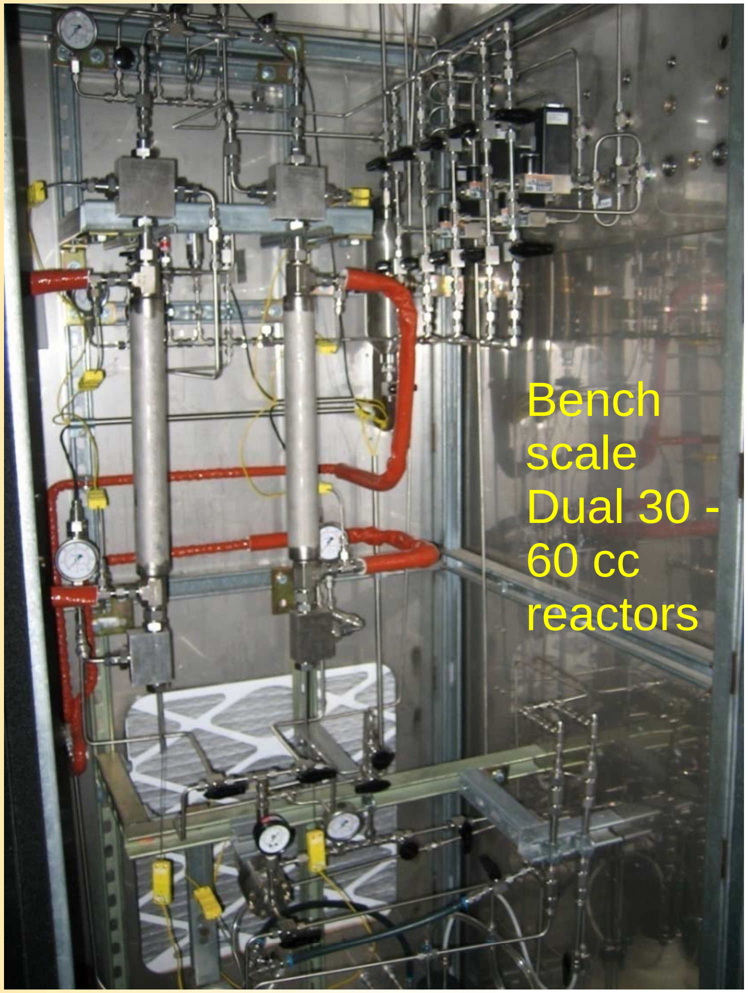
**Flow Reactor**
- Sixteen continuous flow reactors.
  - 0.05 – 1.5 mL of catalyst
- Four independently controlled temperatures
- 30 - 500°C operating temperature
- 0 - 2000 psig operating pressure
- Four gas feeds
- Three liquid feed pumps

# Catalyst Testing Reactors

## Process Demonstration– Bio-Based Products
## Batch and Flow Reactors

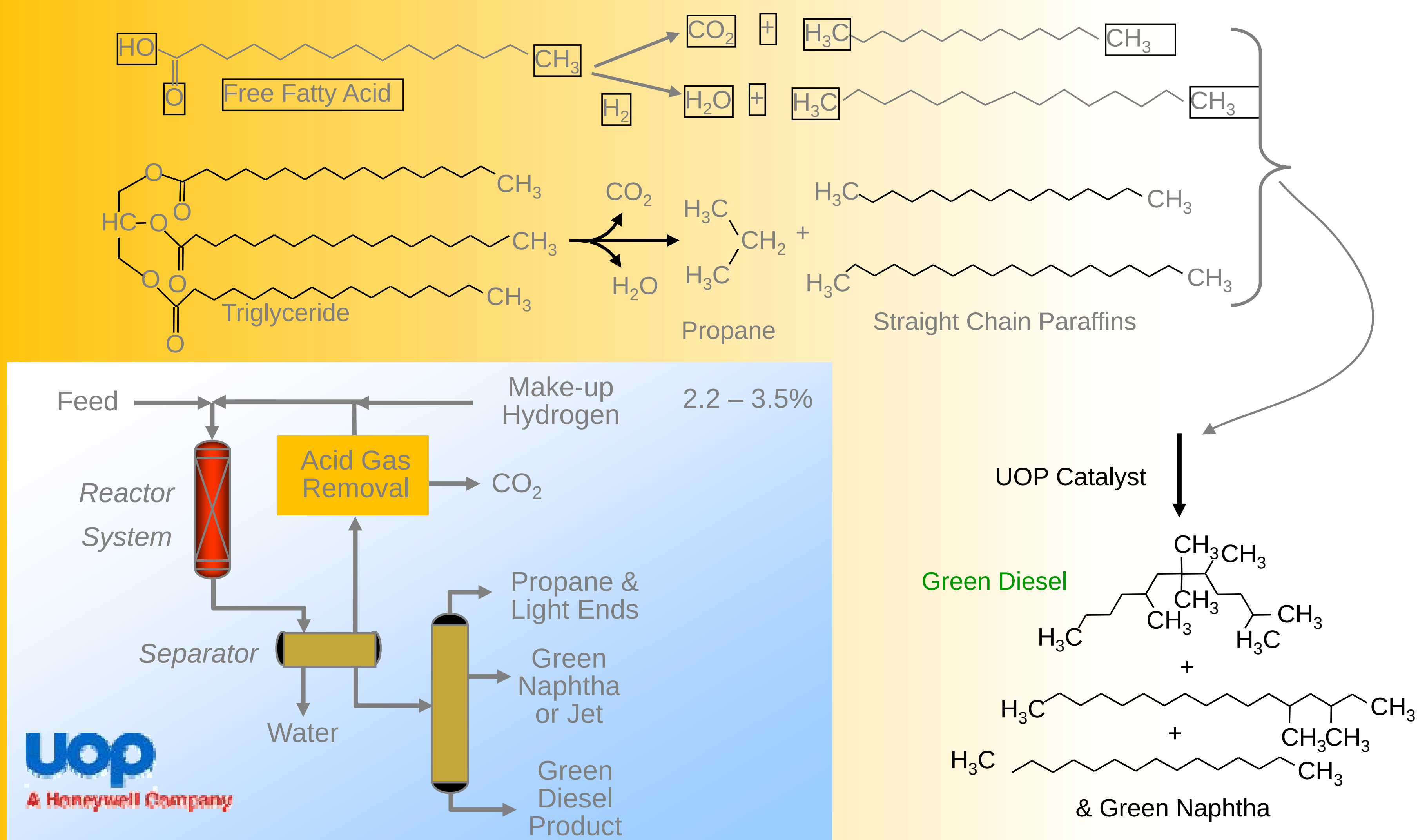
### Flow Reactors

- **Catalyst Bed volume 1mL to 1L**
- **Liquid and low temperature melting solids (~100°C)**
- **Continuous gas and liquid feed**
- **Long-term unattended operation**

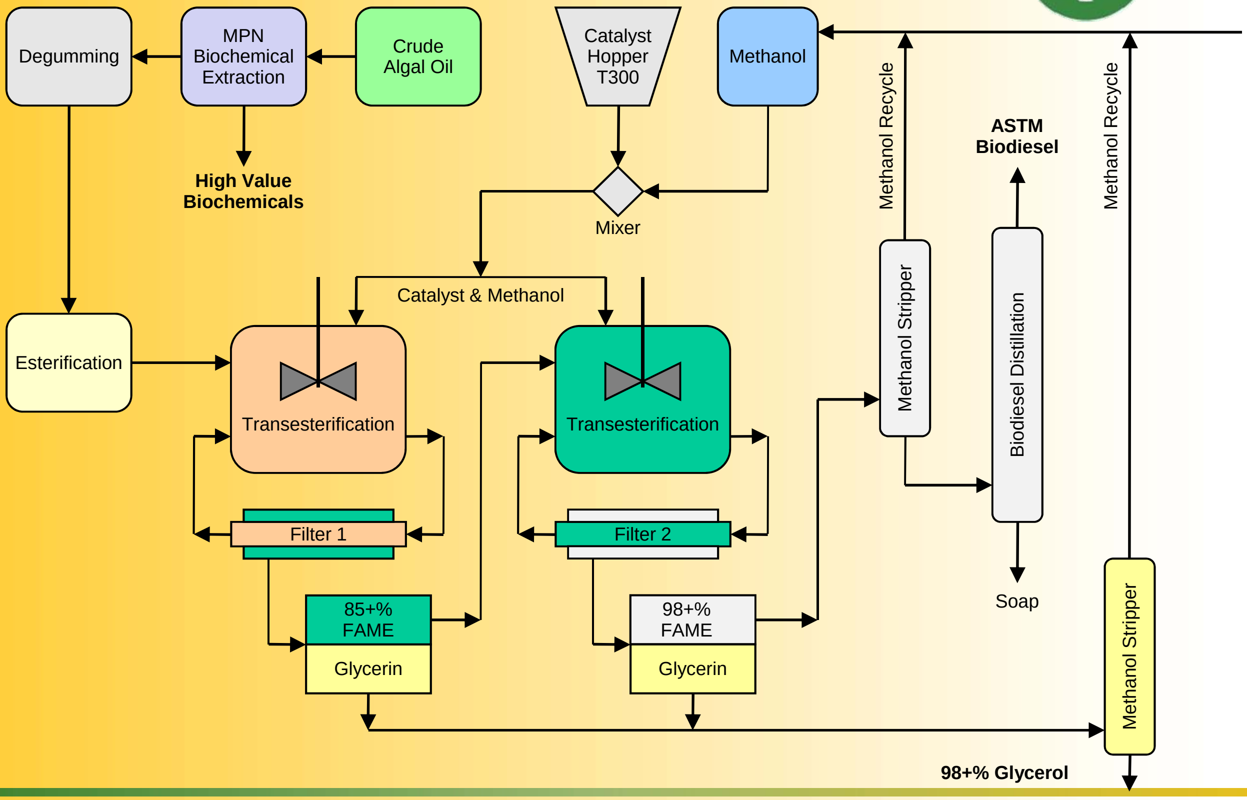
# Ecofining Chemistry & Simplified Process Diagram

*Product is a High Quality Pure Hydrocarbon known as Green Diesel*



# T300 Heterogeneous Catalyst

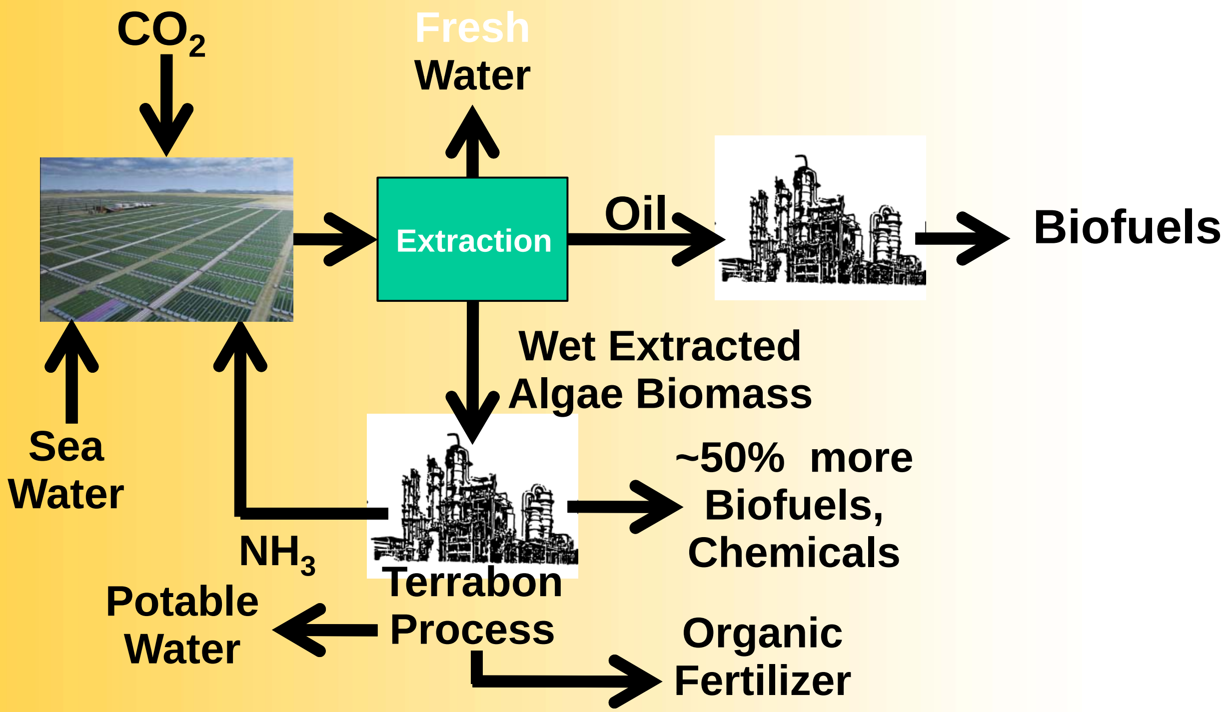
- Granular solid with an APS of 12-20 µm.
- Surface area of 15 $m^2$/gr and density of 2.6 gr/ml.
- High attrition resistance.
- Non-hazardous for low cost disposal

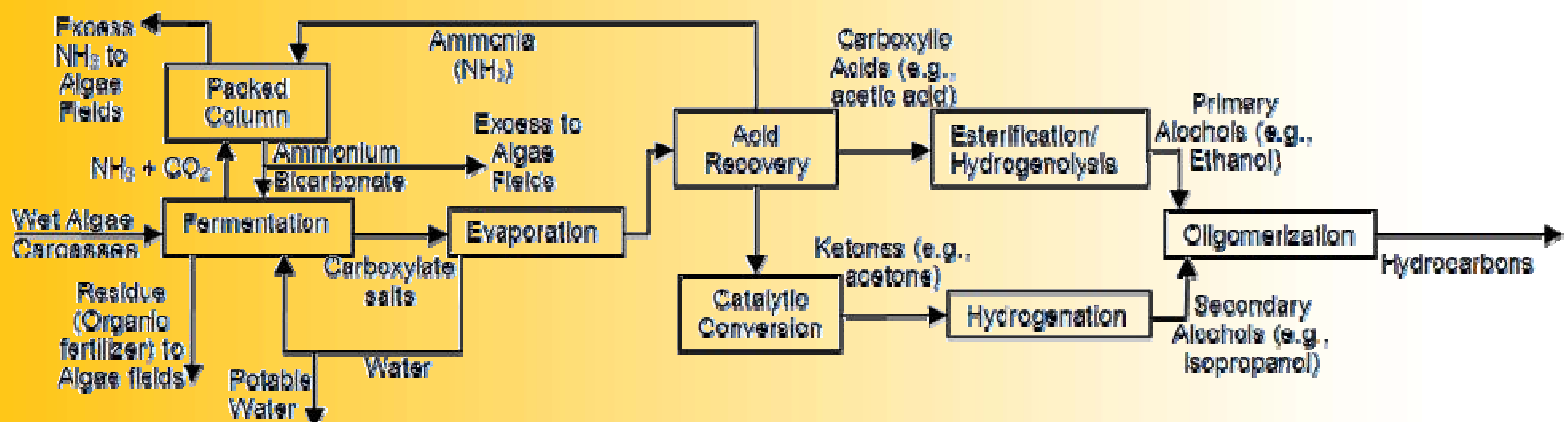



# Fermentation to Fuels

NAABB National Alliance For Advanced Biofuels and Bio-products

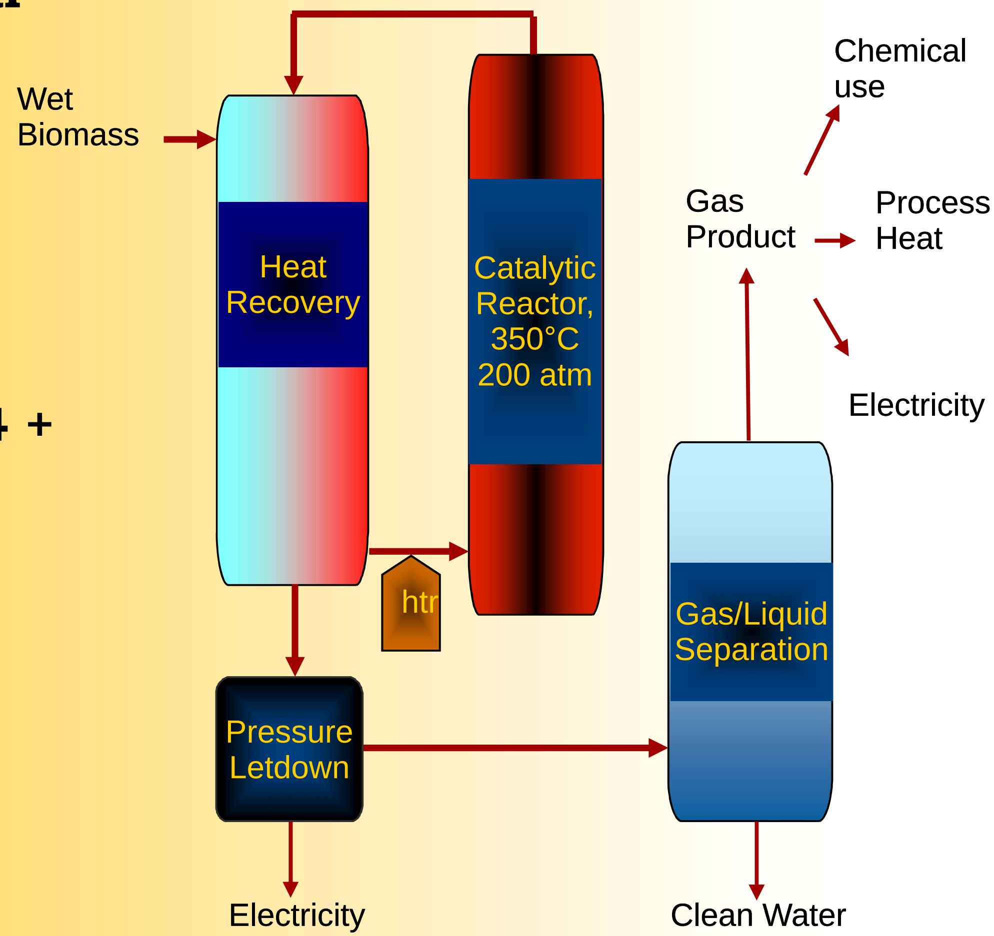
TERRABON



# Catalytic Hydrothermal Gasification

- low-temperature, single-step synthetic natural gas from wet waste
- metal catalyst
- high-pressure steam reforming & methanation
- $C_xH_yO_z + nH_2O \rightarrow aCH_4 + bCO_2$
- Equilibrium Control of Gasification



# Skid-Mounted Gasifier Test Unit – Pilot

NAABB
National Alliance For Advanced Biofuels and Bio-products

- **Current design for Pilot Plant will gasify 10 metric tons of wet biomass/day at 15% solids**
- **This size will produce 500 $m^3$ (18,000 $ft^3$) of net methane (after internal use) per day**
  - This amount of methane will power a 100 kWe generator 24 hours/day
  - Or could store gas and generate 200 kWe for 12 h/d
- **At 30 $g/m^2/d$ productivity, algae feedstock would require 4.5 ha (11 acres) of ponds**

Genifuel

- **If harvest 2 t/d dry algae with 25% lipids, then:**
  - Lipid production is 500 kg/d, or 143 gal/d
  - Lipid-Extracted Algae (LEA) is 1.5 t/d dry mass
- **CHG will yield 500 $m^3/d$ net product methane from 1.5 t/d dry LEA mass**
- **Value of the products:**
  - Lipid value @ $3.00/gal = $429/d
  - Methane generates electricity worth $261/d
- **Therefore, CHG increases biofuel value by 60%**

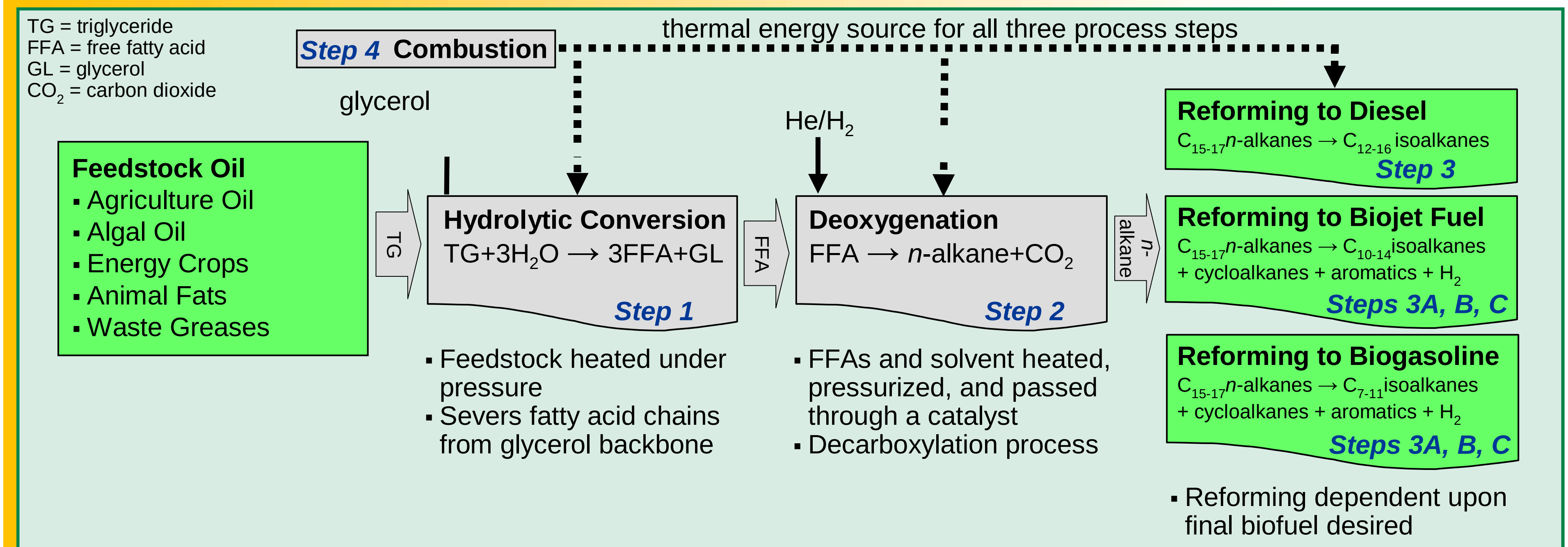
# Centia™ Renewable Petroleum Process

## Catalytic conversion of oil-rich feedstocks to fungible (drop-in) fuels

- Uses little net hydrogen – not a hydrotreating approach

## Combustion of glycerol for heat source increases energy efficiency

## Production of aromatics directly reduces cost and produces $H_2$



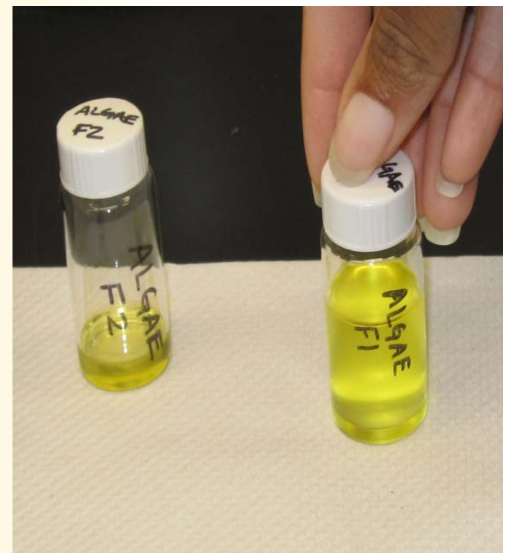
# Preliminary Fast Pyrolysis Results

| Temperature | Biooil Heating Value (Btu/lb) | Heating Value (in MJ/kg) |
|---|---|---|
| 400$^{o}$C | 15,609 + 657 | 36.2 + 1.5 |
| 500$^{o}$C | 15,956 + 408 | 37.0 + 0.95 |


Fractionation set-up

**Results of simple distillation and fractionation of algal biooil samples.**

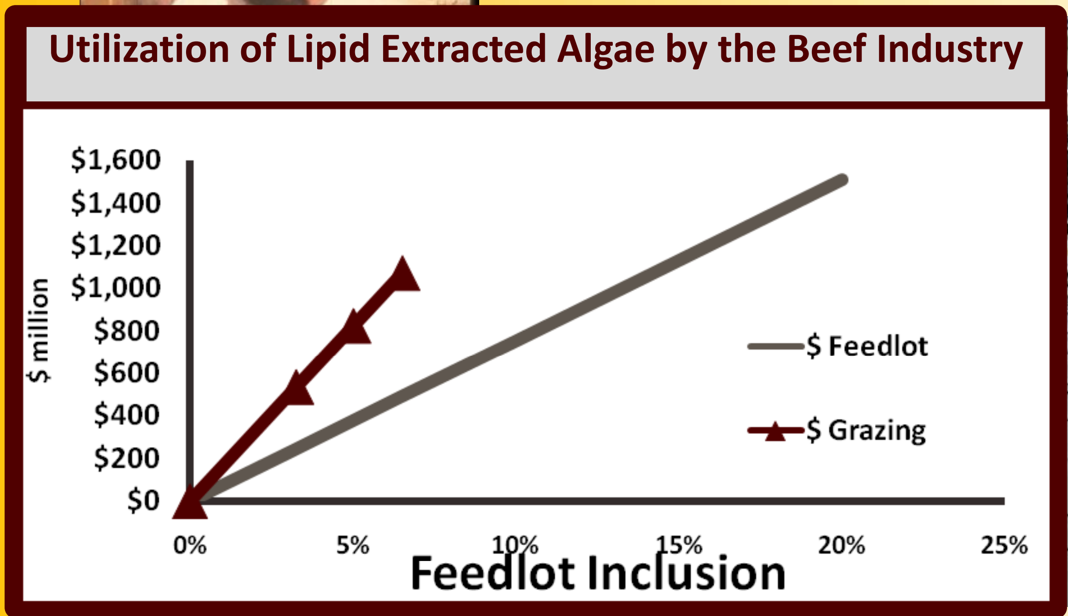
| Chemical Family | Relative (%) |
|---|---|
| Alkanes | 44.53 |
| Alkenes | 22.00 |
| Acids | 22.44 |
| Ketones | 2.44 |
| Alcohols | 3.83 |
| Heterocyclics | 2.32 |
| Nitriles | 0.71 |




Algae Biooil Fractionates (40-75$^{o}$C)

# Animal and Mari-culture Industry

Amino acid content
Digestibility coefficient
Biological value
Net protein utilization
Protein efficiency ratio
peptides, carbohydrates, lipids, vitamins,
pigments, minerals and other valuable trace elements



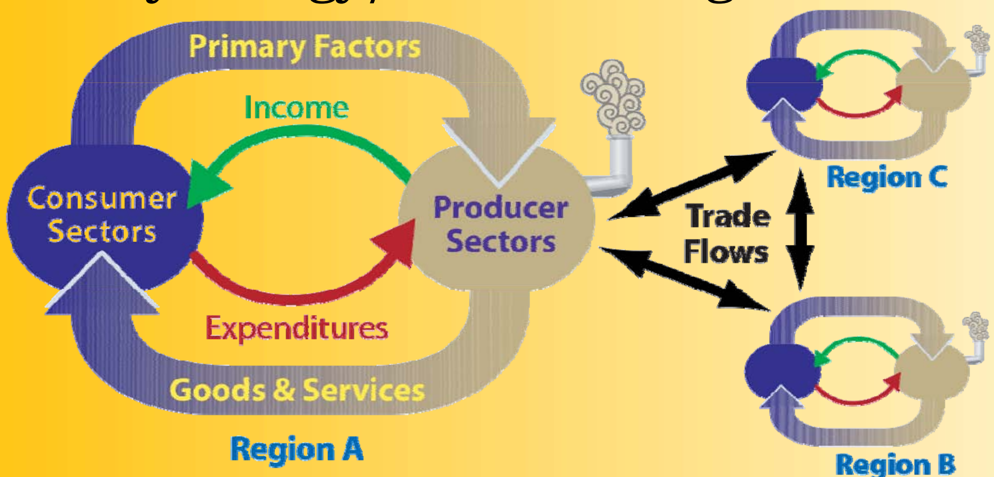

Donald Danforth Plant Science Center — Discover • Enlighten • Share • Nourish
Los Alamos National Laboratory Est. 1943

Pacific Northwest National Laboratory — Proudly Operated by Battelle Since 1965
U.S. Department of Energy

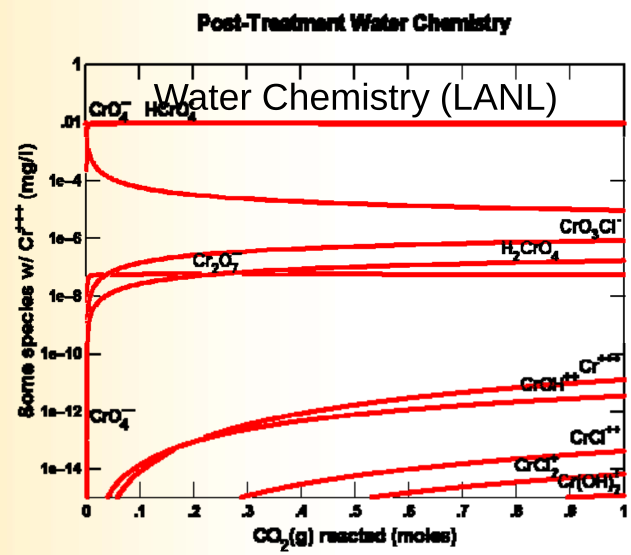
# Sustainability

## Quantitatively assess the energy, environment, economic viability and sustainability of approaches to guide our strategy

- **Economic analysis** • Economic models • Global analysis • LCA an Process Analysis
- **Resource Management** • CO2 management • Hydrology/water management

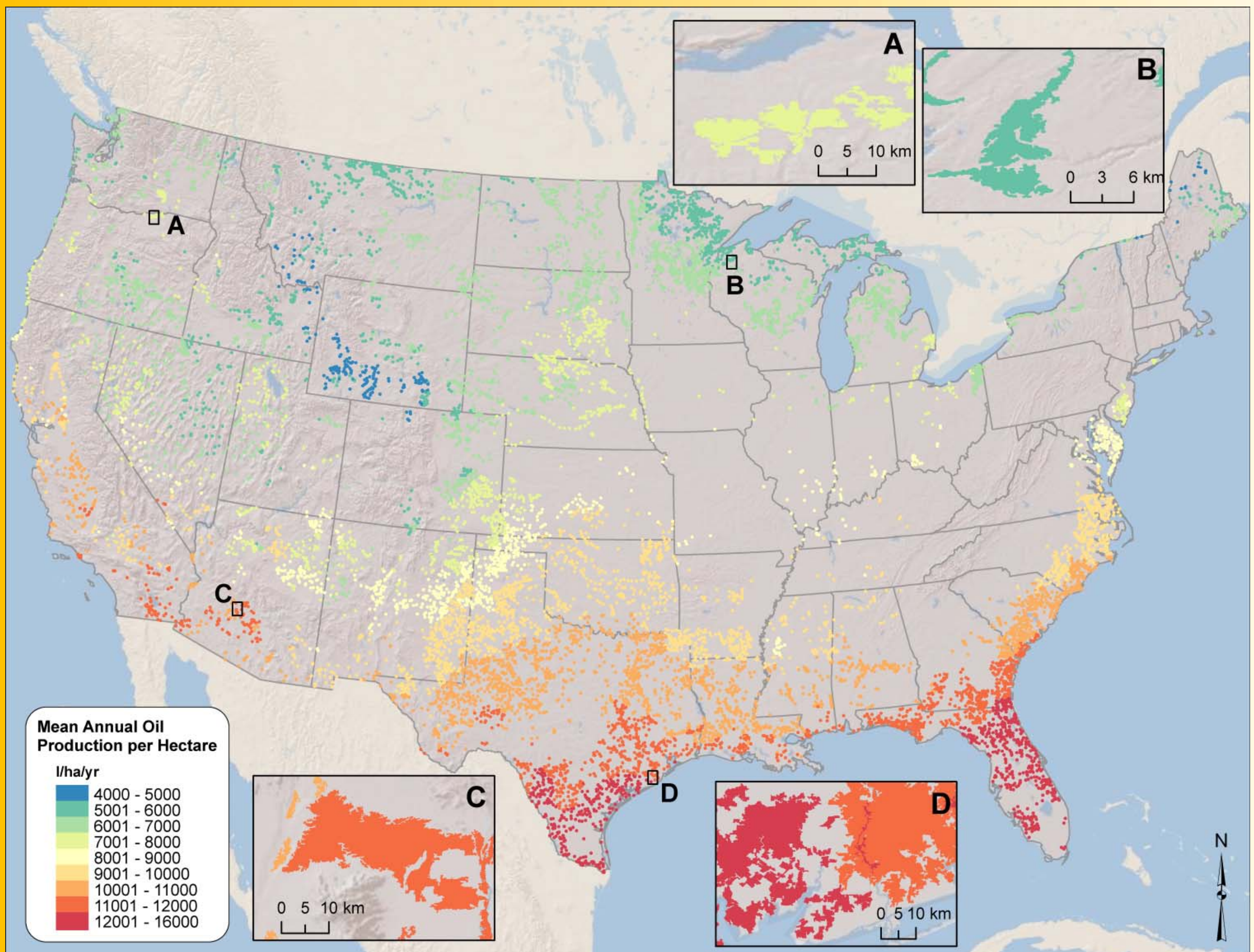


Computable General Equilibrium Model (TAMU)



Water Chemistry (LANL)

# NAABB Sustainability Modeling



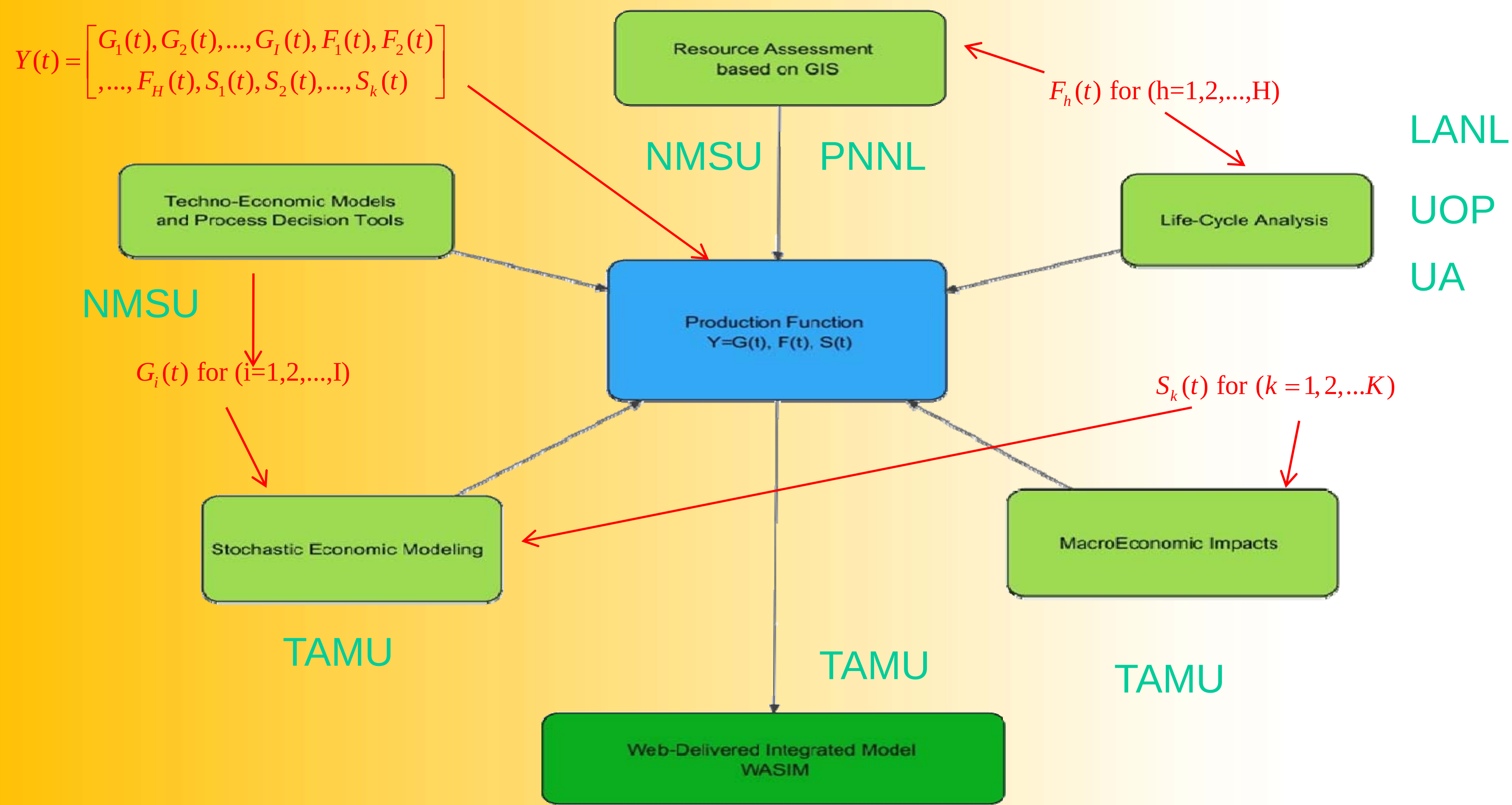

NAABB is building a comprehensive model that end-users can access via the web to answer questions like:

- How much algae can I produce in Nevada in December?
- Is it profitable for me to become an algae farmer with 1,000 acre farm in SE New Mexico?
- How much will a gallon of algal fuel from Florida cost?

# NAABB Approach

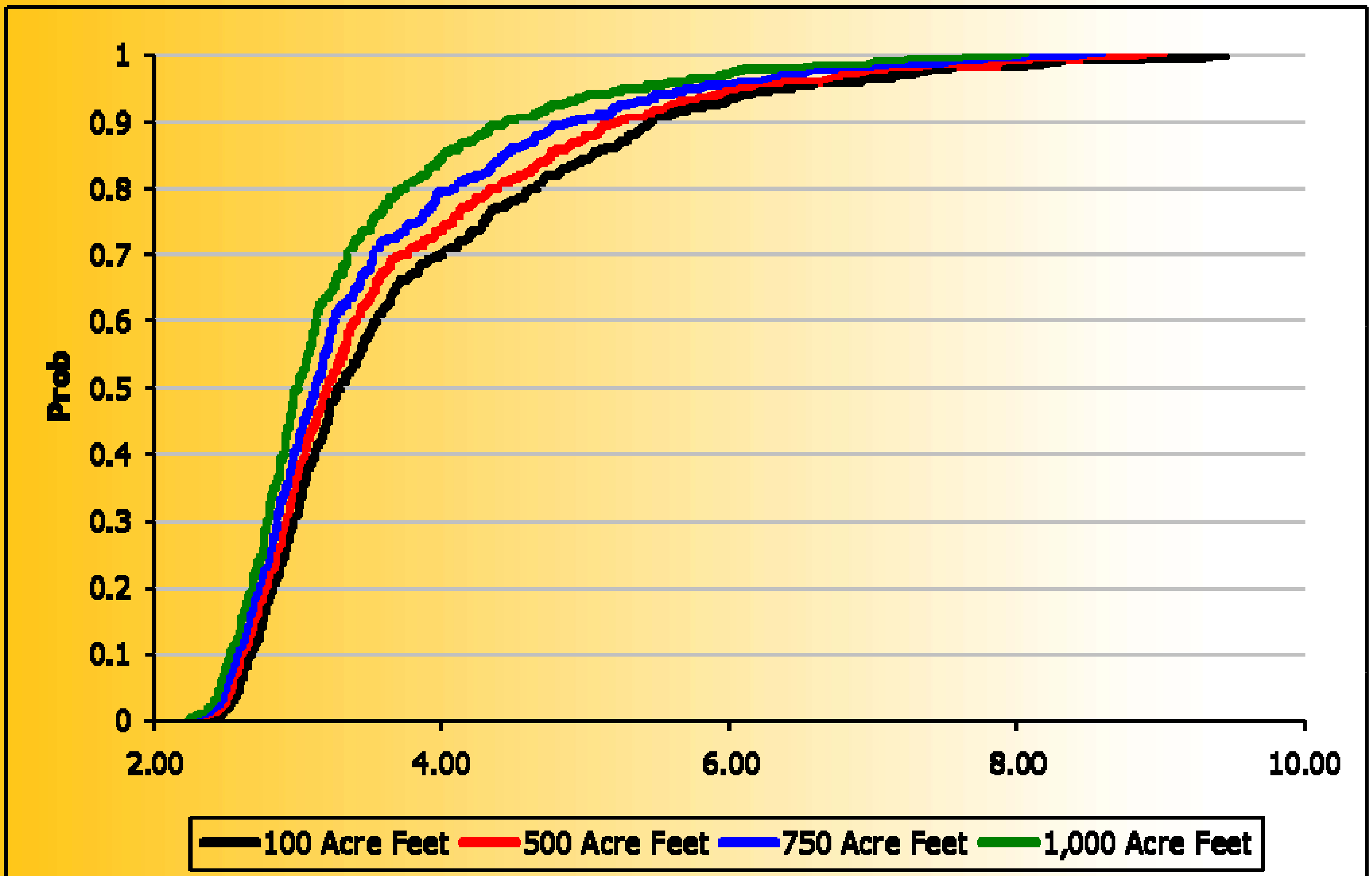
- Integrated experiment and data collection to derive empirical results that drive decision tools and models that address the key E^3 constraints.
- Drive optimization through a "production function" approach.
- Standardization of measurement and reporting
- Risk Analysis using statistical and economic modeling techniques to derive probabilistic ranges around key variables that drive the 'sustainability indices'.
- Comprehensive modeling with team members from engineering, economics, and computer science to build and deliver internal and external decision tools

# NAABB SEP Modeling Schematic



# SEM: Distribution of Total Cost (per gal)

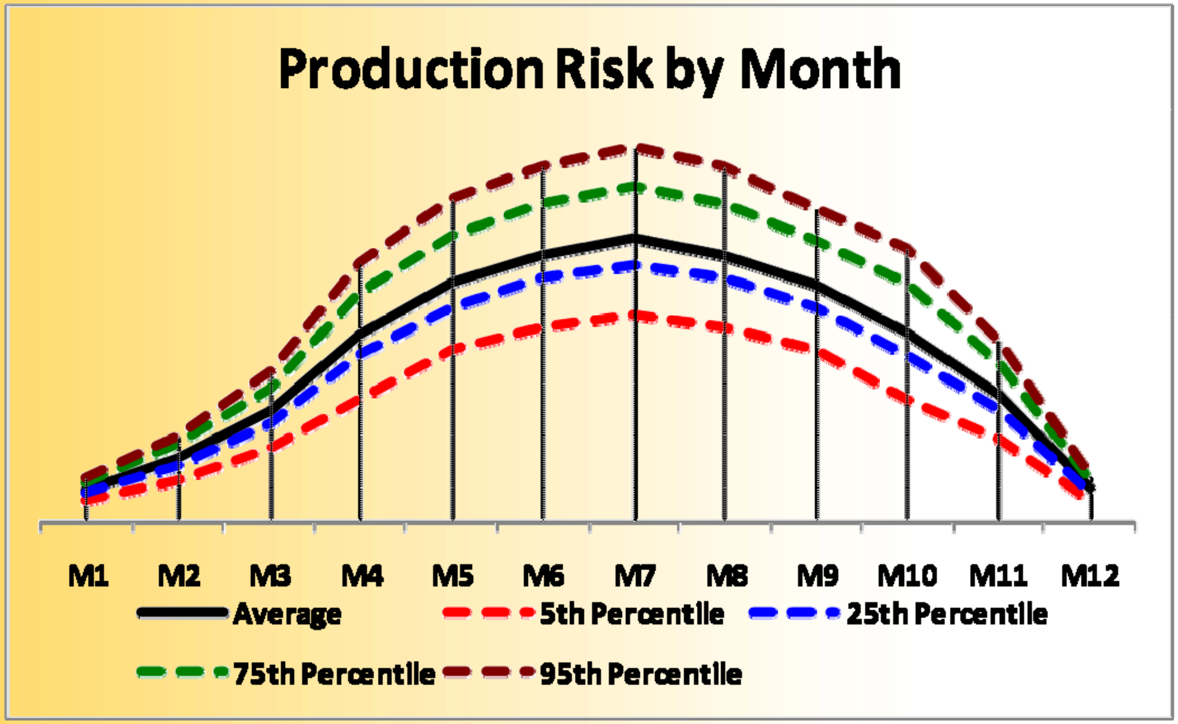
**(TAMU, Richardson et al.)**



# SEM: Distribution of Total Cost (per gal)
**(TAMU, Richardson et al.)**

The sustainability modeling effort will use the production functions and SEP modeling framework (the Y(t) functions) to develop risk profiles of production pathways and to project economic viability.

Monthly production is risky as the confidence intervals suggest



# Sustainability Targets

1. GHG Reduction of a minimum of 60% relative to Petroleum Standard

2. Water Use/Loss in Process and Finished Product less than Petroleum baseline and Corn Based Ethanol Standards

3. Energy Return on Investment > 1

4. Potential for Economic Viability for Firm/Industry (at the Nth level)

| NAABB Deliverables |
|---|
| |
| >50% lipid content at harvest |
| >20g/m2/day biomass yield (open system) |
| 5 g dw/l/day biomass yield (closed system) |
| 5,000 gal/day processing capability for a harvesting unit |
| 15 gal/day lipid extraction capacity per unit |
| Certified Animal Feed |
| LEA $250-1000/ton |
| Glycerol $80/ton |
| $2.10/gal/lipid |
| $0.40/gal processing cost |

$$C(Y_z) = Pelec * Elec + PNutr * QNutr + PWater * QWater + PLabor * Labor + PCarbon * QCarbon$$

# Questions?