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*Title:* LANL's Biofuels Program

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*Intended for:* Multiple Briefings



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## Initiatives in Algal Bio-Fuels

*José A. Olivares  
NAABB Executive Director  
Los Alamos National Laboratory and  
The Donald Danforth Plant Science Center*



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



Slide 1



# U.S. 2008 Transportation Fuel Stats

## U.S. 2008 Transportation Fuel Stats

### Gasoline (cars & trucks)



140 bgy

### Diesel (on-road, rail)



43 bgy

### Aviation (jet fuel)



25 bgy

## US Focus

Technoeconomic Analysis  
Resource Analysis/  
Allocation

Advanced  
Biofuels  
R&D

Algal  
Biofuels  
R&D

Biomass  
Intermediates

Biopower

Cellulosic Ethanol  
RD&D

Sustainability Analysis & LCA

Courtesy of the National Advanced Biofuels Consortium

Locally  
NATION  
EST. 1942

**NAA&BB**  
National Alliance For Advanced Biofuels and Bio-products

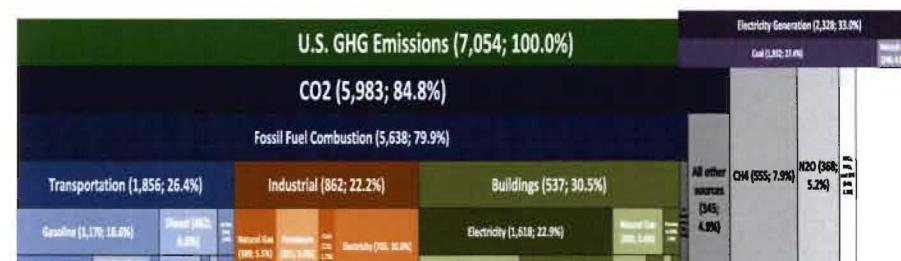
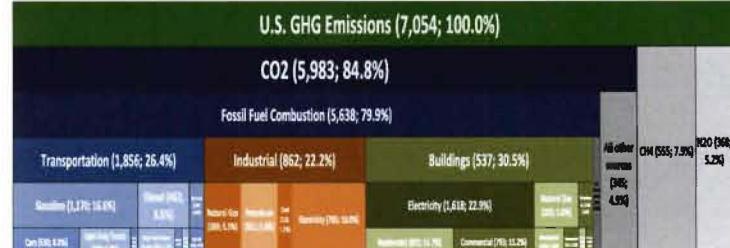
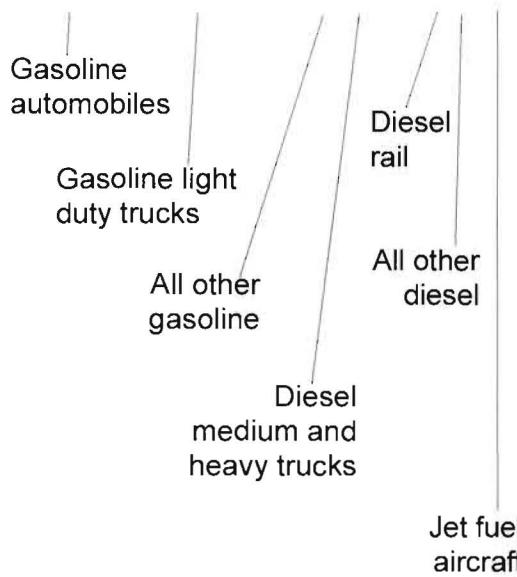
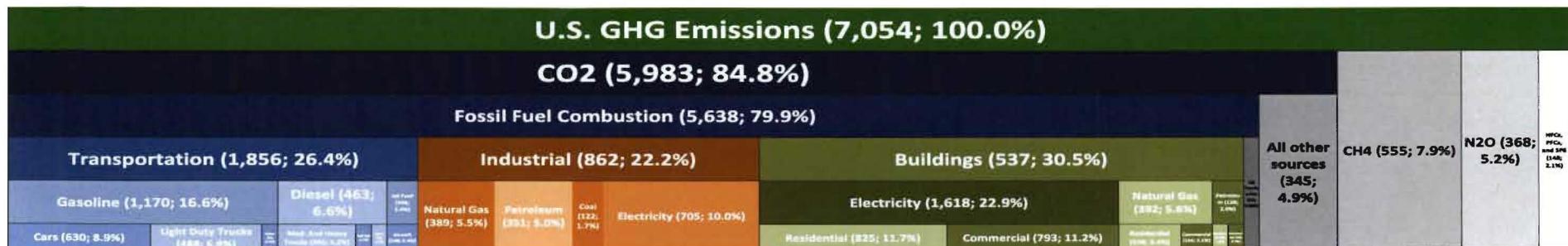
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Slide 2

Biomass  
Biofuels

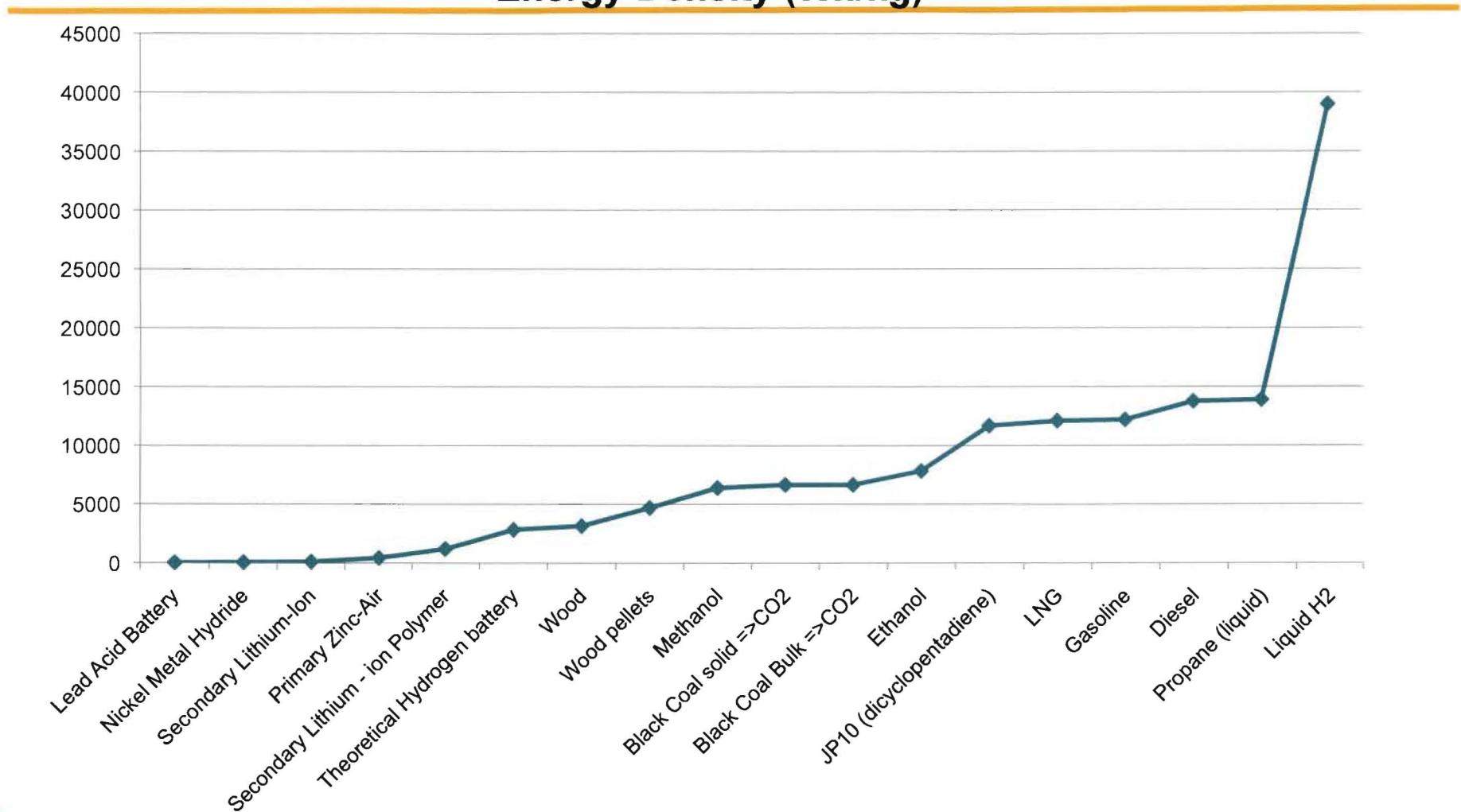
U.S. DEPARTMENT OF  
ENERGY

# Annual GHG Emissions – US Only (Tg CO<sub>2</sub> equivalent, 2006)



Courtesy of the Pacific Northwest National Laboratory

## Fuel and Energy Storage Systems Energy Density (Wh/kg)



# Goal → Algae to Jetfuel



# BIOFUELS FOR THE U.S. MILITARY

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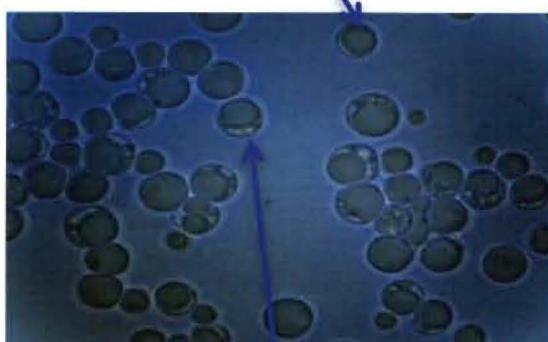


Solazyme Delivers 1500 gal 100% Algal-Derived Renewable Jet Fuel to U.S. Navy



# 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<sub>2</sub>  
Utilize waste water  
Non-food

# Headliner Productivity

## The New York Times Olympic nightmare: A red tide in Yellow Sea

By Jim Yardley

Published: Monday, June 30, 2008

**BEIJING** — With less than six weeks before it plays host to the Olympic sailing regatta, the city of Qingdao has mobilized thousands of people and an armada of small boats to clean up an algae bloom that is choking large stretches of the coastline and threatening to impede the Olympic competition.



Photo Source: AP News Eye Press

- Qingdao, China
- Green alga (*Ulva prolifera*)
- late May - early July 2008
- > 200,000 tons biomass
- < 17 km<sup>2</sup> coastal area  
(~ 4,200 acres)



> 47 tons/acre

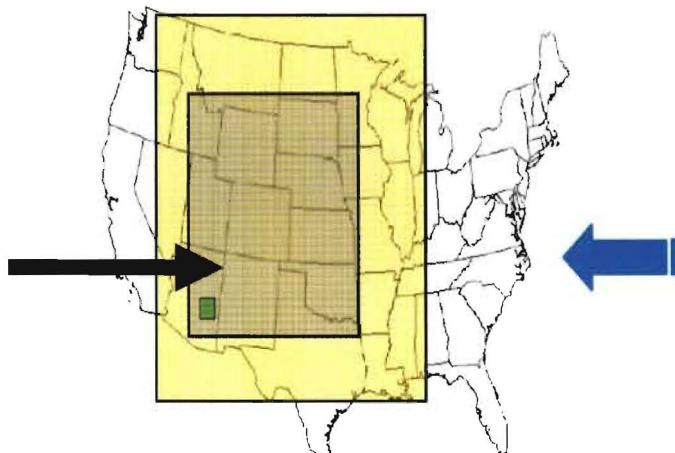


# The Promise of Algae-Based Biofuels

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

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

Figure courtesy of Sandia National Laboratory



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

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

Corn  
Soybean  
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 CO<sub>2</sub> and recycles carbon for fuels and co-products



# Technical Challenges

## Biology and Cultivation



- Cultivation system design
  - Temperature control
  - Invasion and fouling
- Cultures
  - Growth, stability, and resilience
- Input requirements
  - CO<sub>2</sub>, H<sub>2</sub>O 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 gasifier being used by a NAABB partner to convert algal biomass to fuels



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



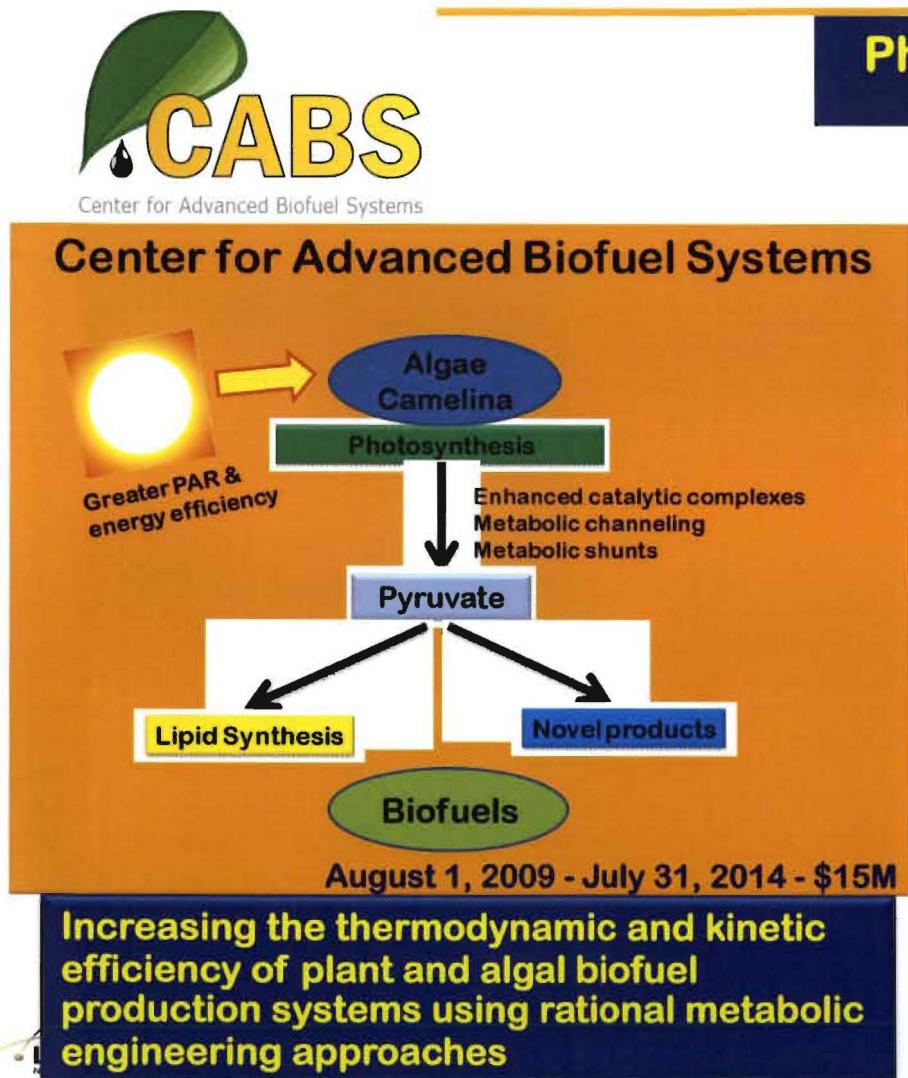
## Conversion and End-use

A nano-membrane filter being developed by a NAABB partner

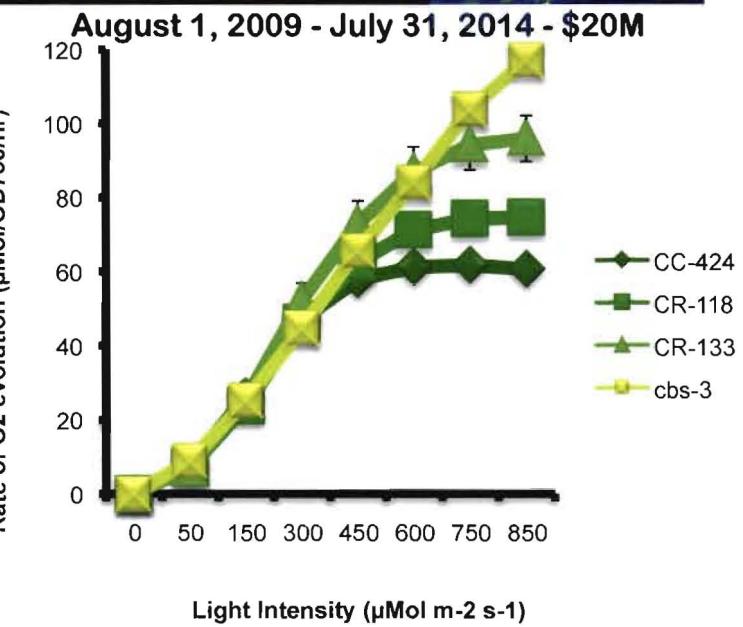
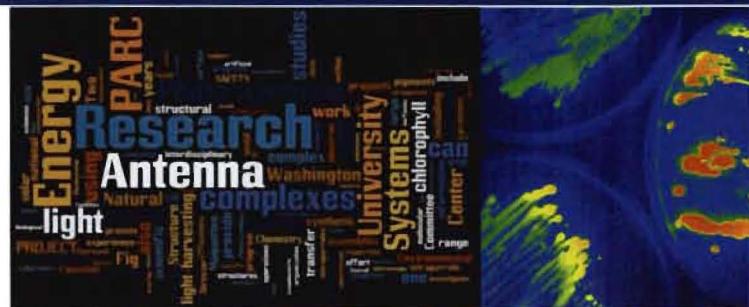
Slide 10



# DOE- Office of Science - Energy Frontier Research Centers



## Photosynthetic Antennae Research Center Optimizing light harvesting efficiency



# US DOE – ARPA-E Projects



*The miracles of science*

Butamax<sup>™</sup>  
Advanced  
Biofuels LLC

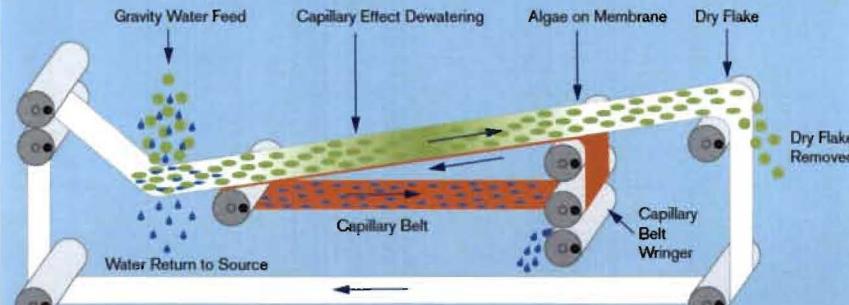


MacroAlgae Butanol -  
Isobutanol from Seaweed



AlgaeVenture Systems Harvester

Separates algae from water, dewatering, dries



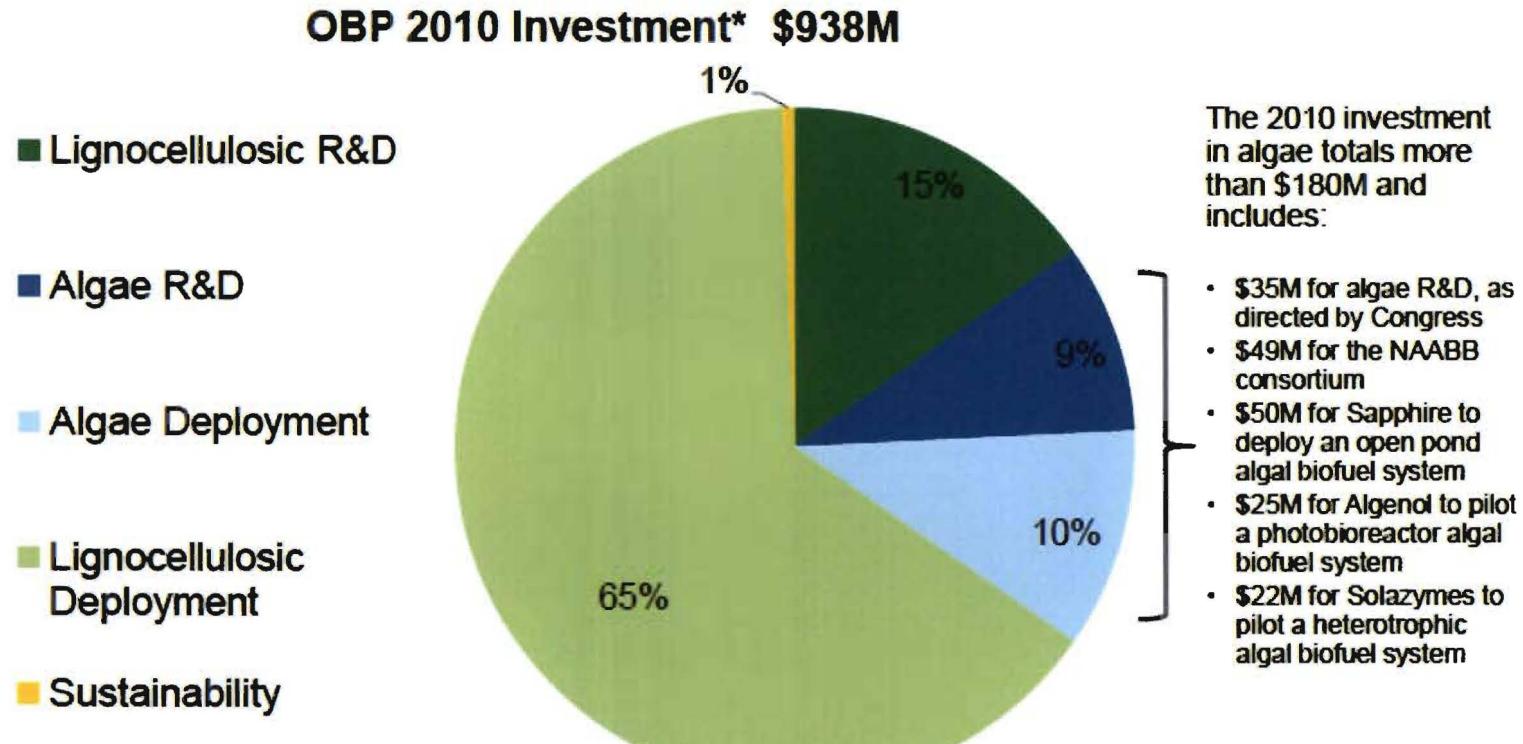
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U.S. DEPARTMENT OF  
**ENERGY**

# Office of Biomass Programs Investments



\*Includes regular FY2010 appropriations and 2009 ARRA funds

# US DOE Algal Biofuels Consortia

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- New algal harvesting technologies
- Pilot-scale cultivation test beds
- Animal feed for the aquaculture industry.
- \$9 M Federal



**Sustainable Algal Biofuels Consortium**  
*cultivating energy solutions*

- Biochemical conversion
- Physical chemistry properties of algal fuels and fuel intermediates
- \$6 M Federal

## Consortium for Algal Biofuels Commercialization

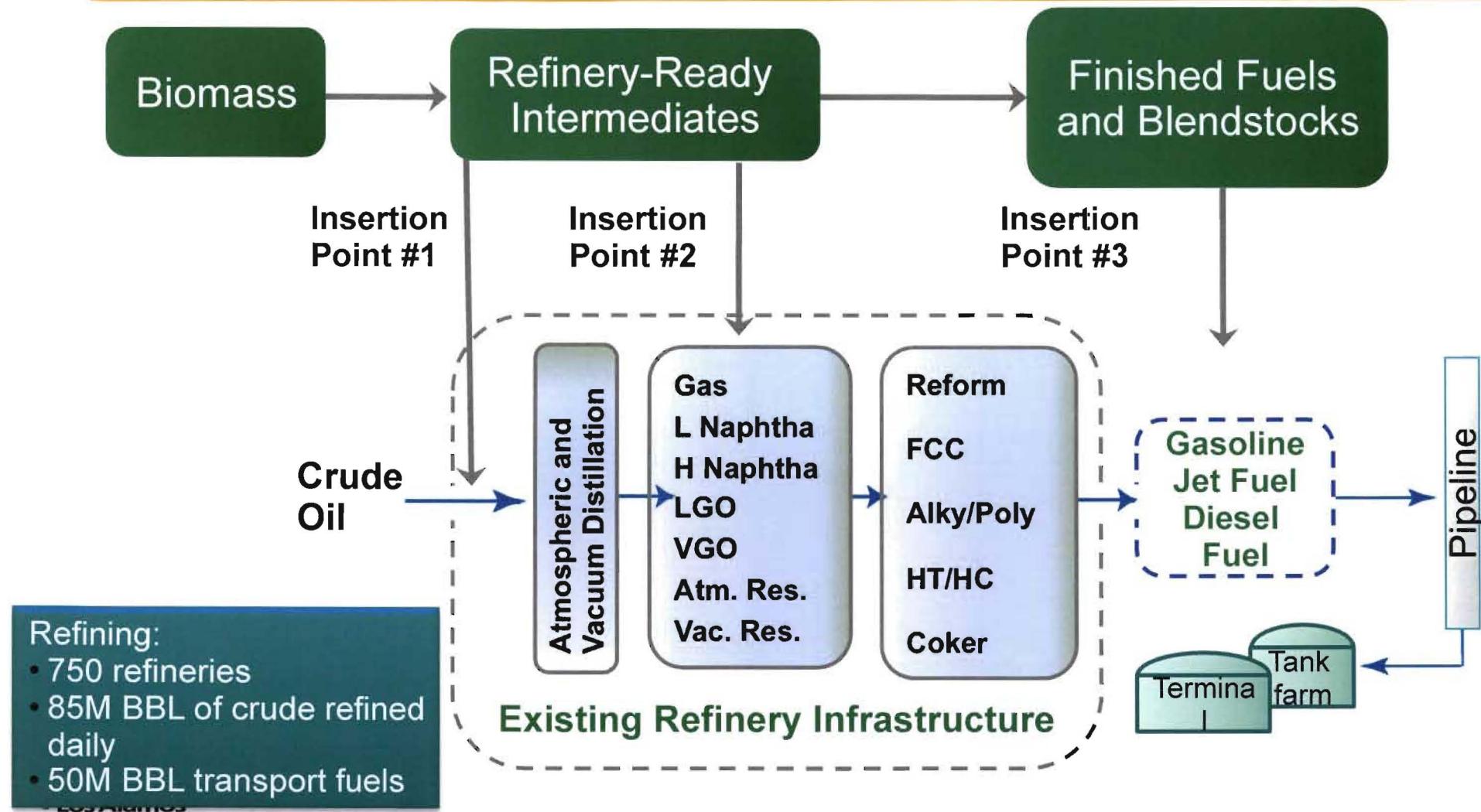
- Crop protection
- Algal nutrient utilization and recycling
- Genetic tools
- \$9 M Federal



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**Aim: Use Current infrastructure to Produce and Transport Biofuels**

\$35M Federal + \$11M Cost Share



NATIONAL LABORATORY  
EST. 1942

## Algal Biology

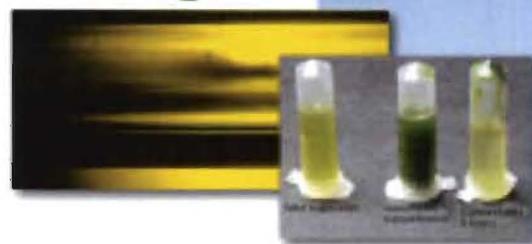


### Greater space-time lipid/algae yields

## *Cultivation*



## ***Harvesting and Extraction***



## Novel techniques to reduce cost and environmental impact



CO<sub>2</sub>



## Water



## Land



## **Valuable Coproducts**



## Livestock feed

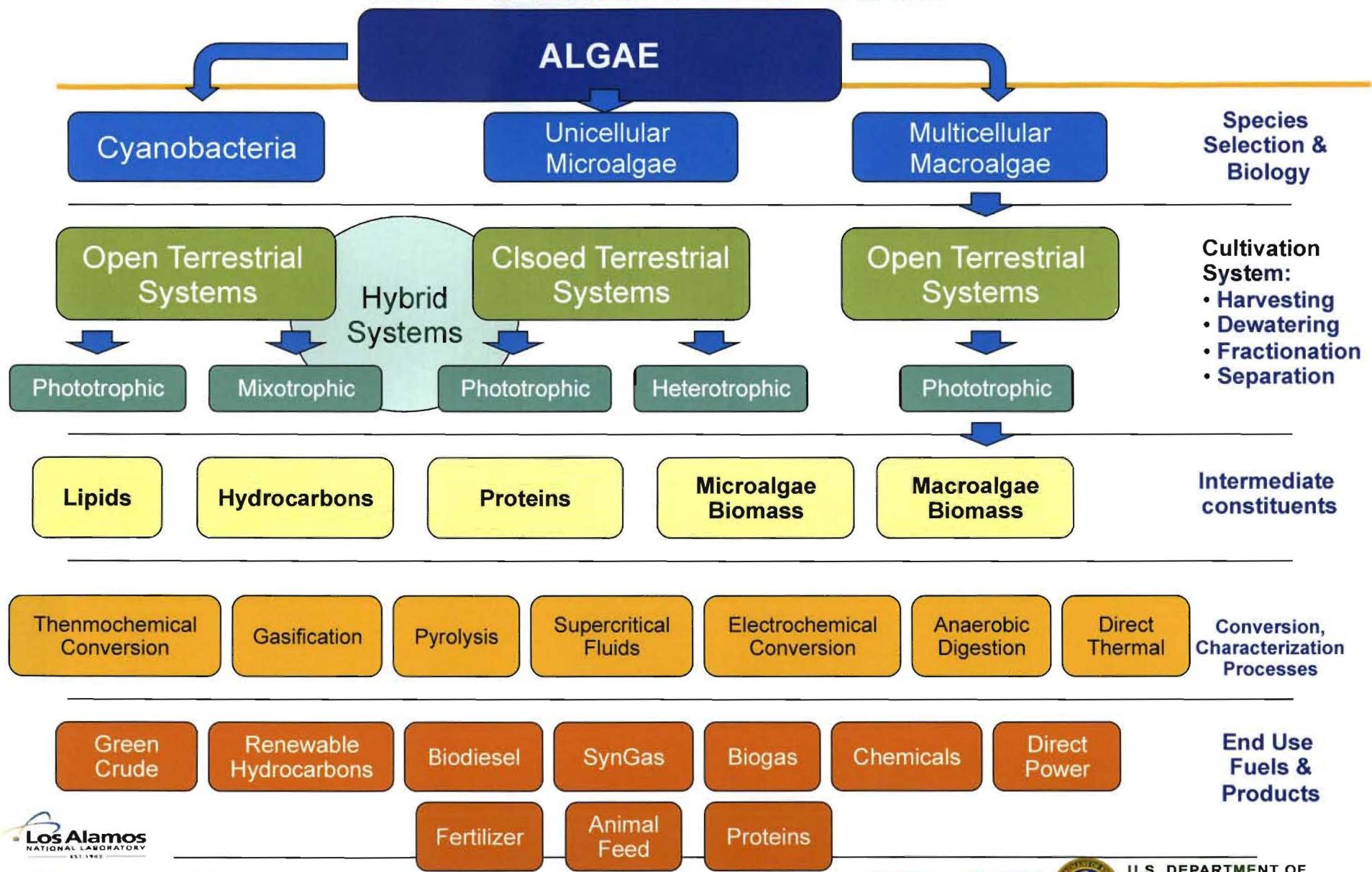
## Direct energy production

## ***Fuel Conversion***

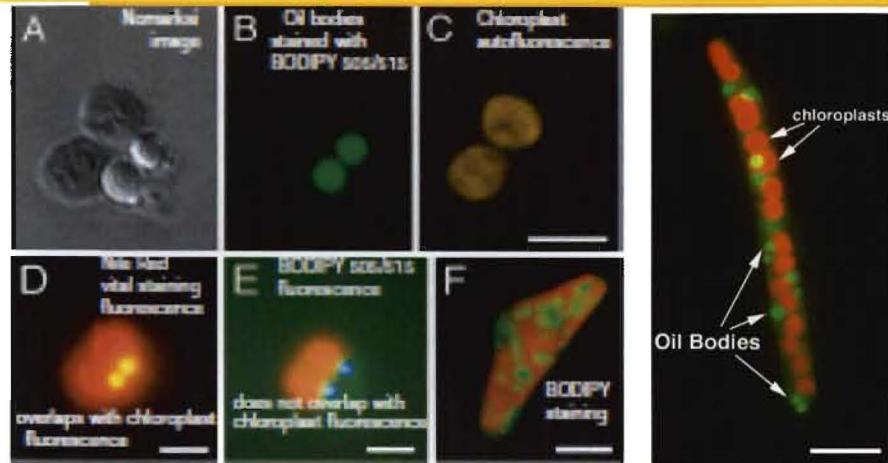


## High energy-density fungible fuels

# NAABB RESEARCH, DEVELOPMENT AND DEPLOYMENT PROGRAM

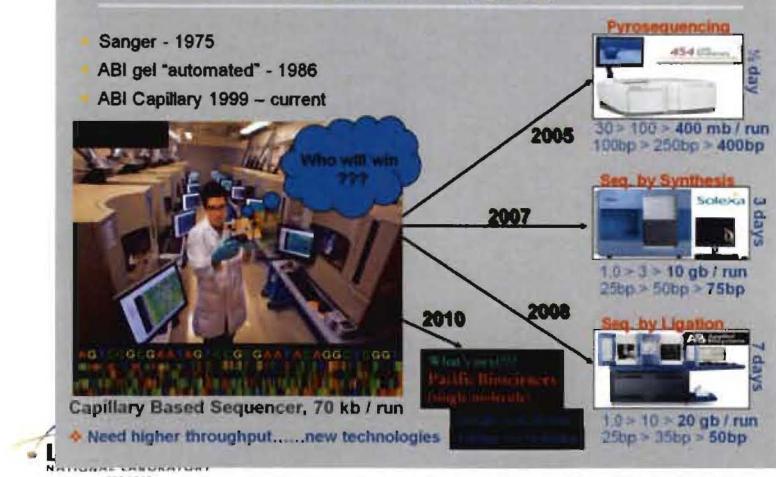


# ALGAL BIOLOGY



## Phenotypic and Genotypic Analysis

### Automated DNA Sequencing Technologies Present ---> Future



### GOALS:

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

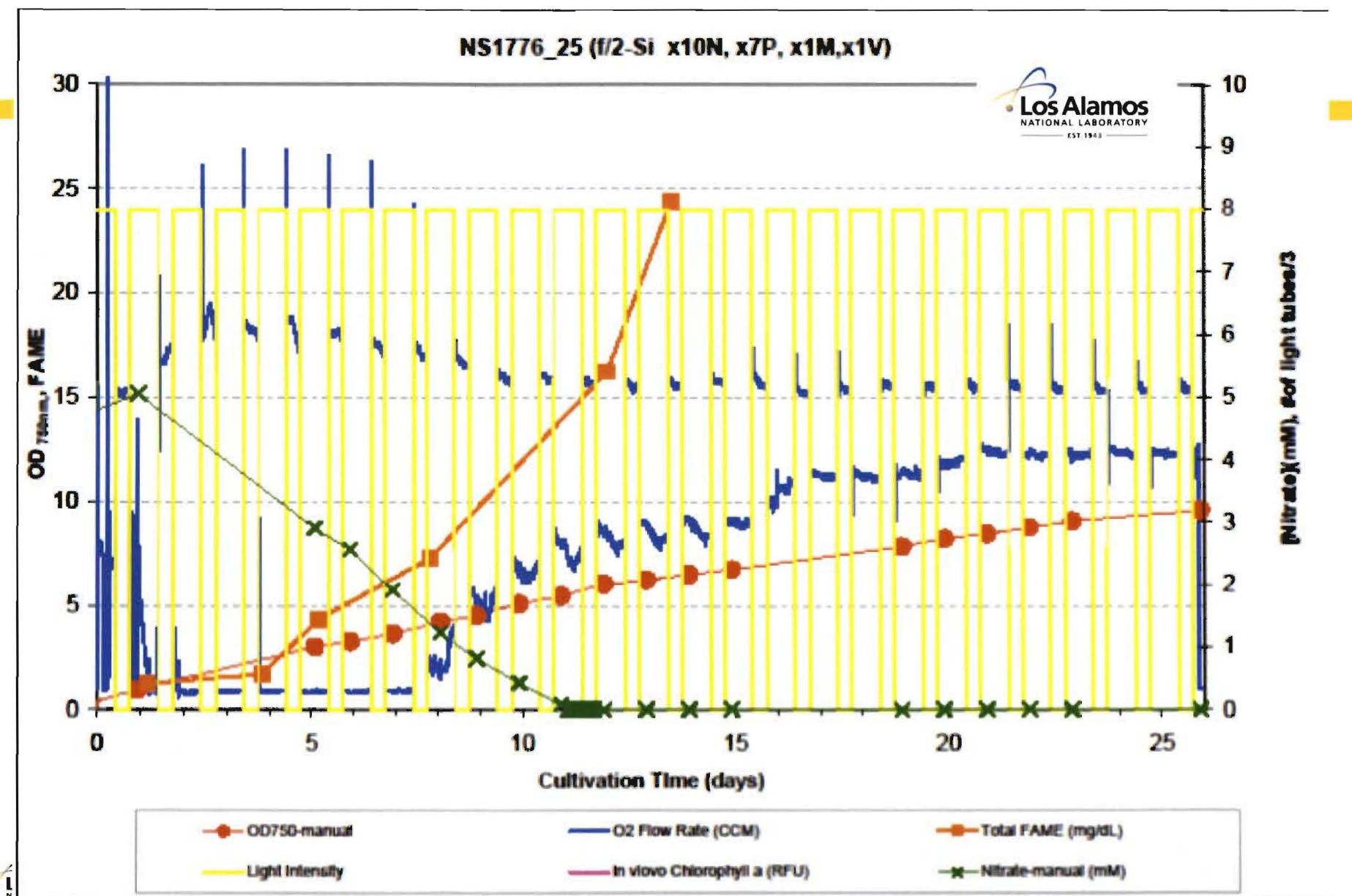
### Systems Biology

- Sequencing/Transcriptomics/Proteomics
- Mutagenesis
- Genetic modification

### Model & Production Organisms:

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

## Oxygen consumption by bacteria in bioreactor culture of NS 1776



# 16S RNA Analysis Results of NS1776 Culture

## 100% Genus Identity

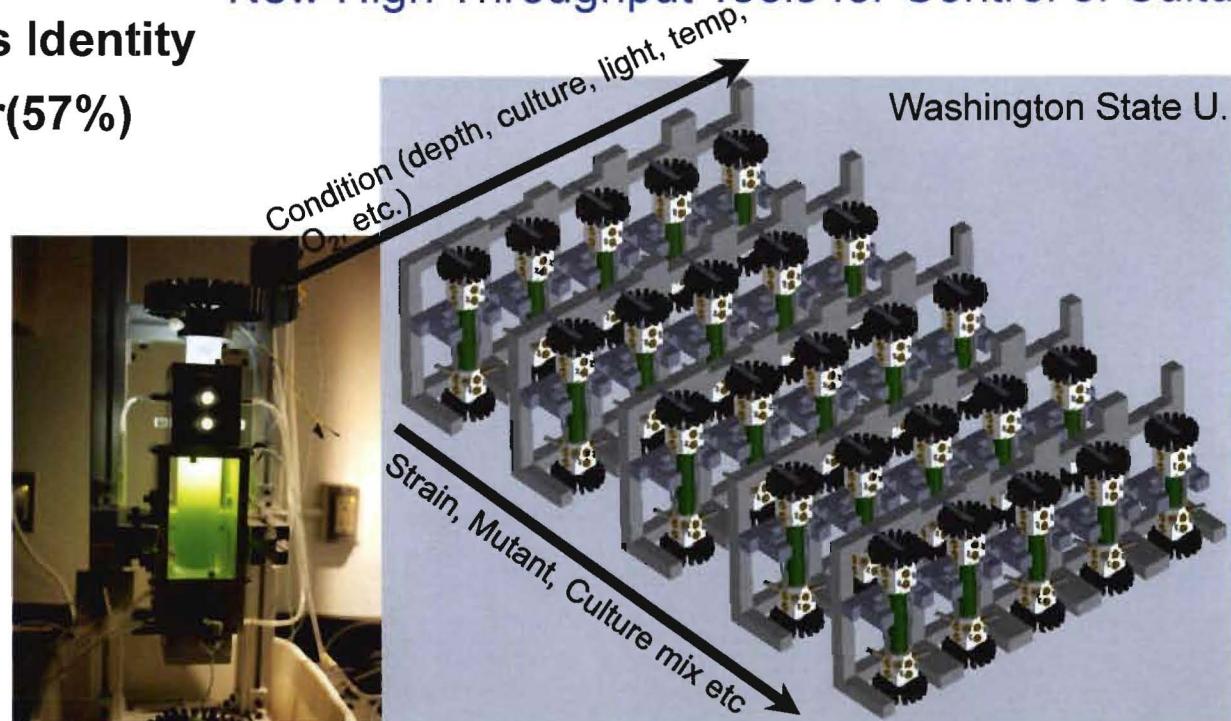
- **Algoriphagus**
- **Marinobacter**
- **Limnobacter**

- Marinobacter has ability to degrade hydrocarbons
- Limnobacter can oxidize thiosulfate
- Haliscomenobacter has ability to breakdown sludge

## Less than 100% Genus Identity

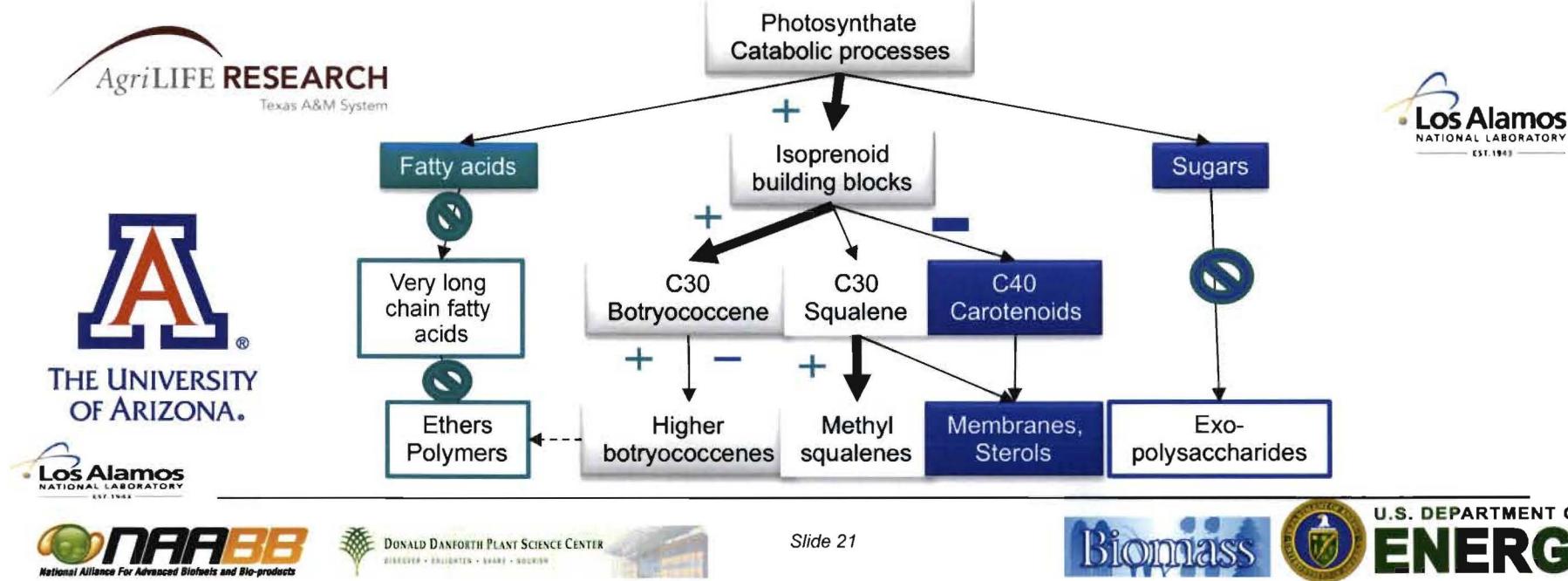
- **Haliscomenobacter(57%)**
- **Oceanicola(67%)**
- **Tateyamaria(78%)**
- **Henriciella(88%)**

## New High Throughput Tools for Control of Cultures



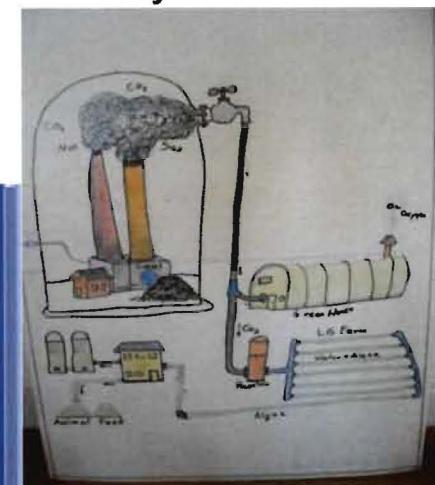
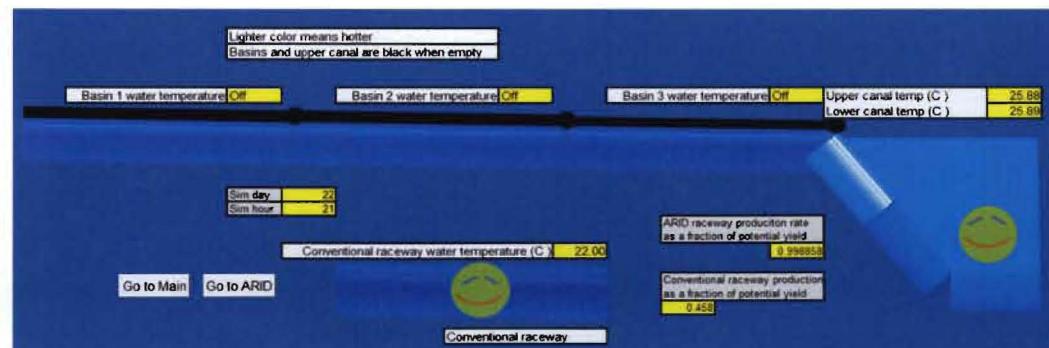
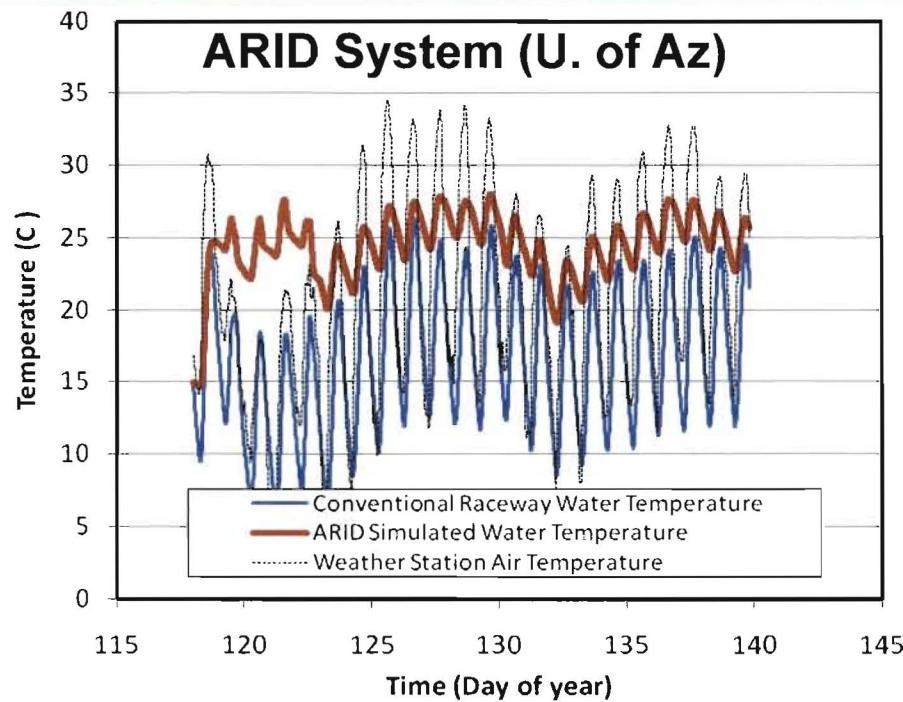
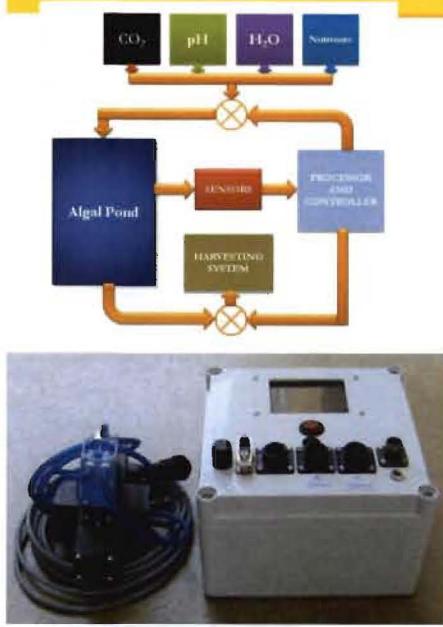
# Algal Genetics, Selection, and Manipulation

- 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.

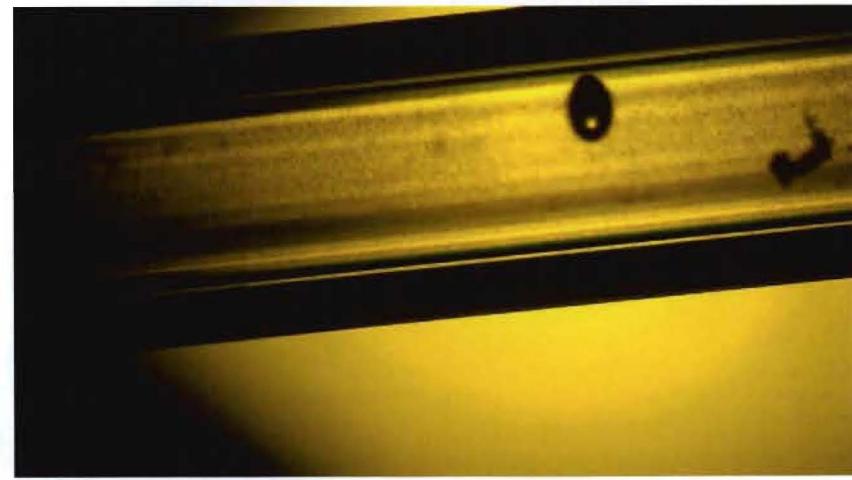
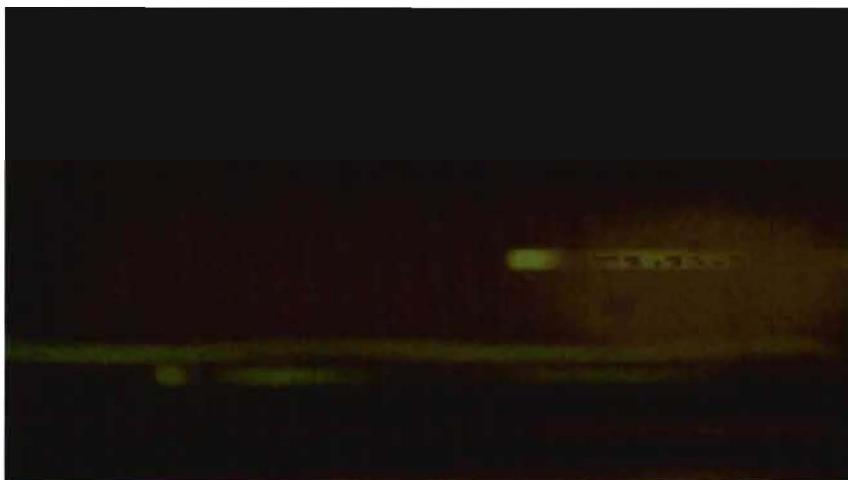
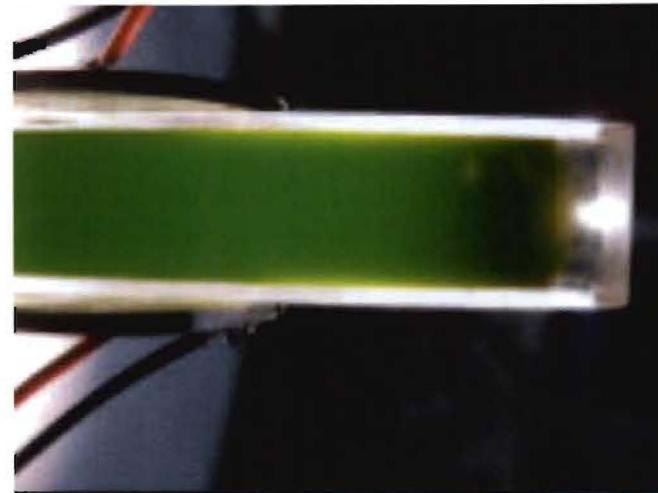
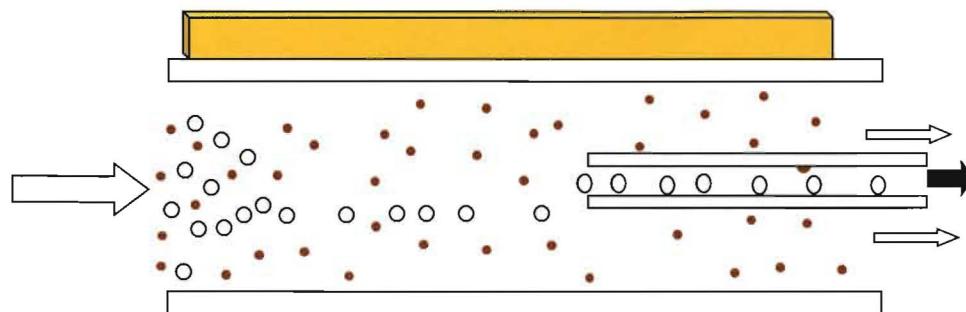


# Cultivation – Productivity, Environment, Nutrients, Water

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

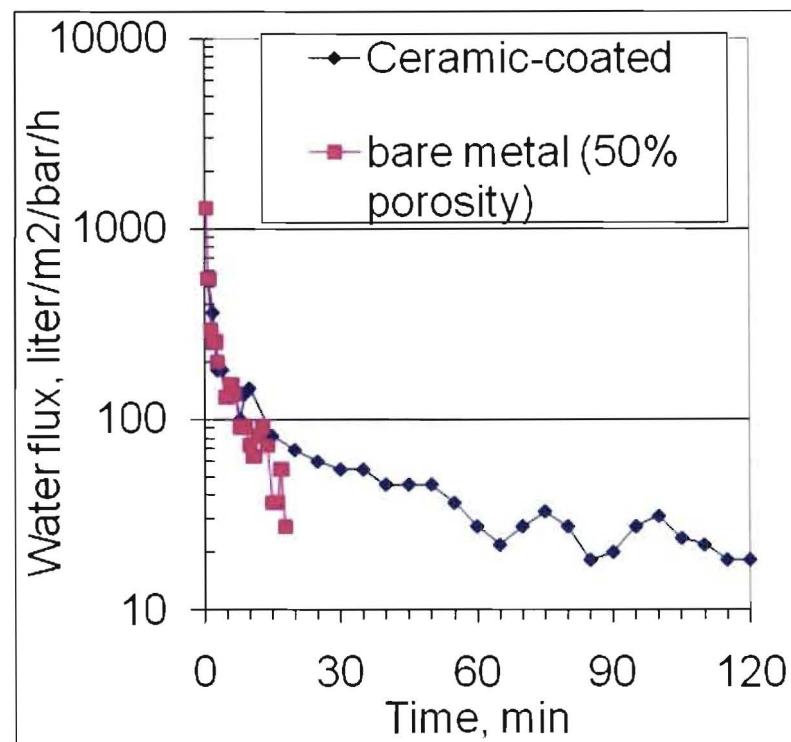
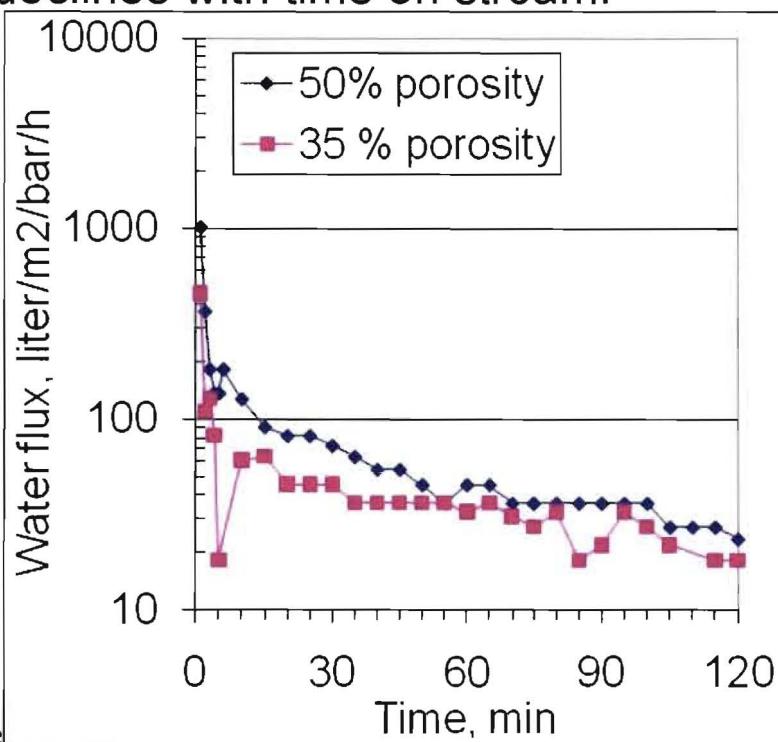
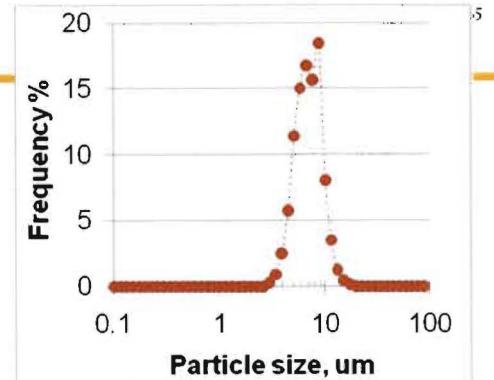


## Acoustic Concentration of Algae from Culture Medium Los Alamos National Laboratory (2010 R&D 100 Winner)

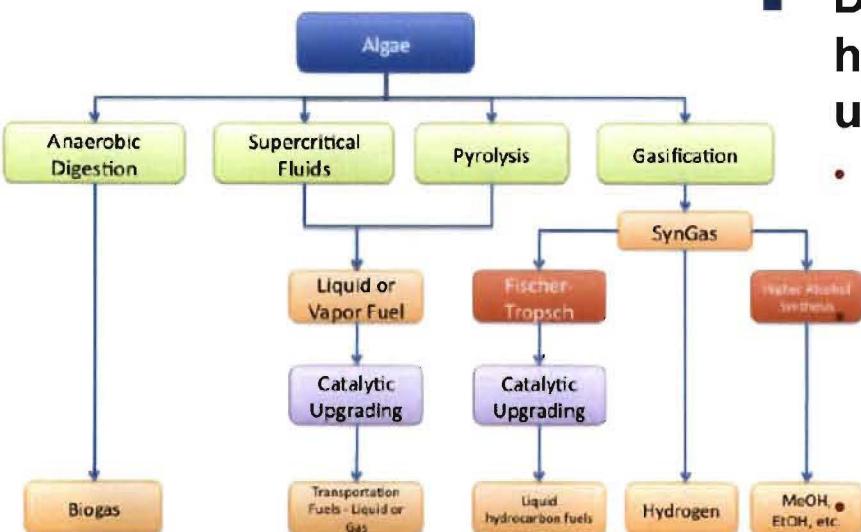


# Preliminary testing results of an algae culture solution

- Filtration under a constant  $\Delta P$  at very low surface velocity ( $\sim 0.03\text{cm/s}$ ).
- Algae particles (2 to 20 $\mu\text{m}$ ) 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

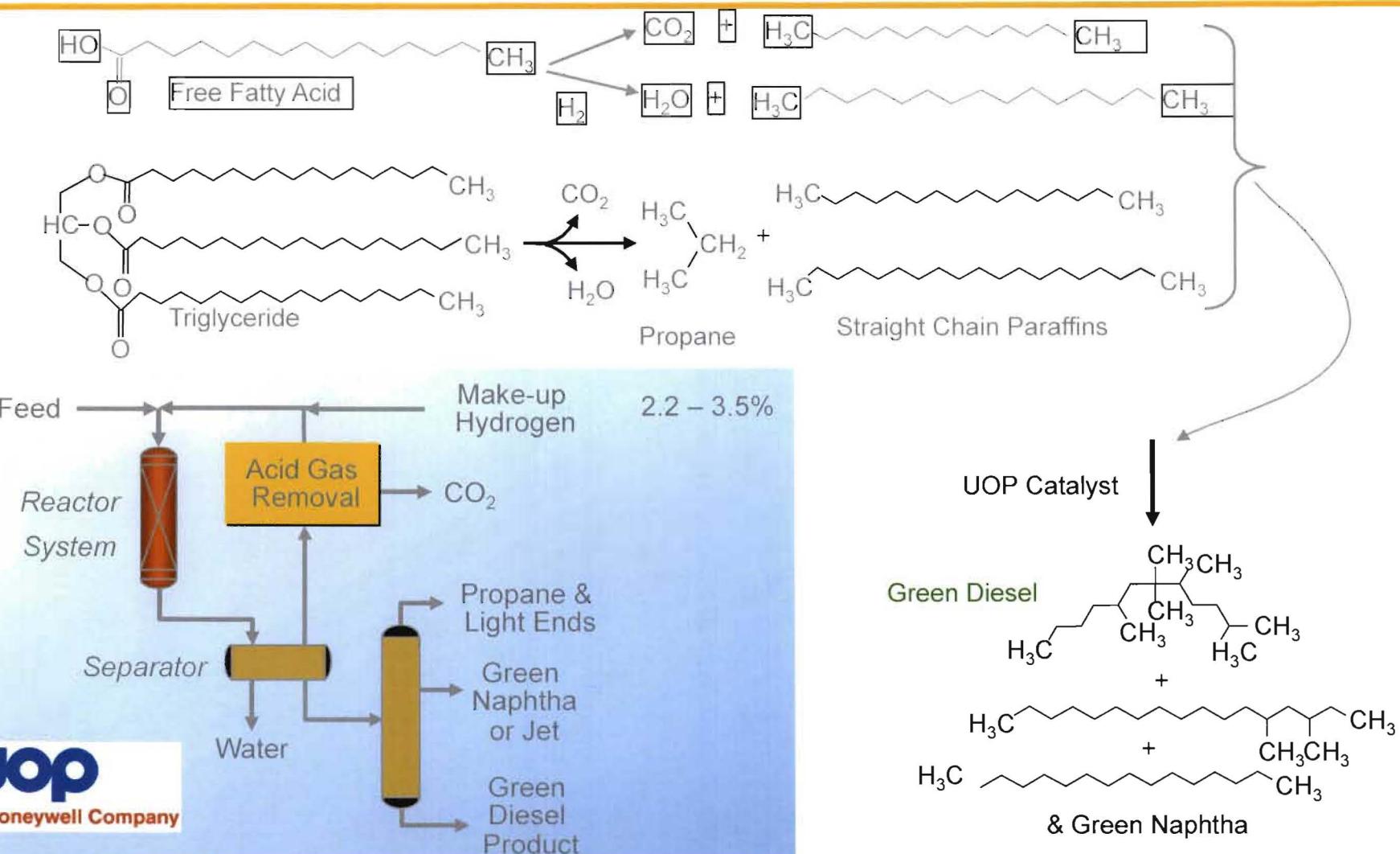
**Biomass conversion to fuels** • Catalytic gasification • Thermochemical gasification and power • Fast pyrolysis and hydroprocessing • Anaerobic fermentation to EtOH and gasoline

**Fuel characterization** • Physical and chemical properties of algal esters and biofuels • Thermophysical and transport properties of biofuels



# Ecofining Chemistry & Simplified Process Diagram

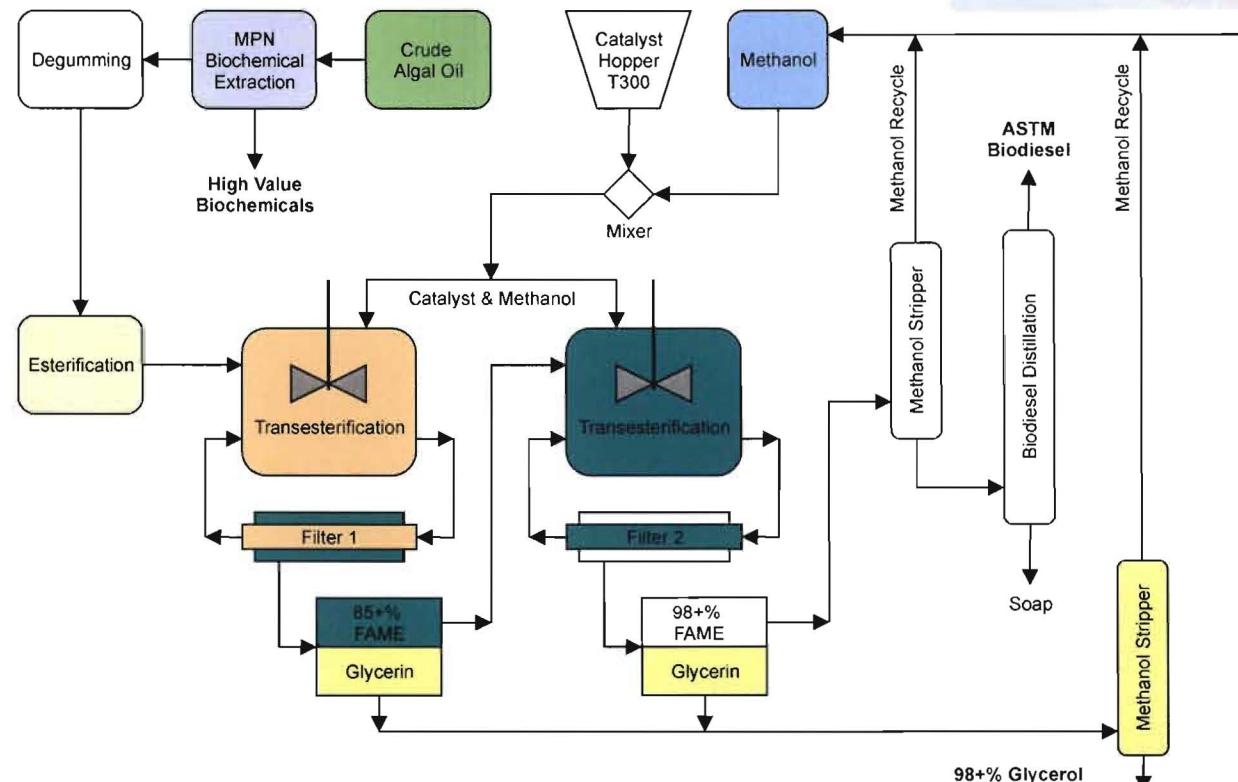
*Product is a High Quality Pure Hydrocarbon known as Green Diesel*





# T300 Heterogeneous Catalyst

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



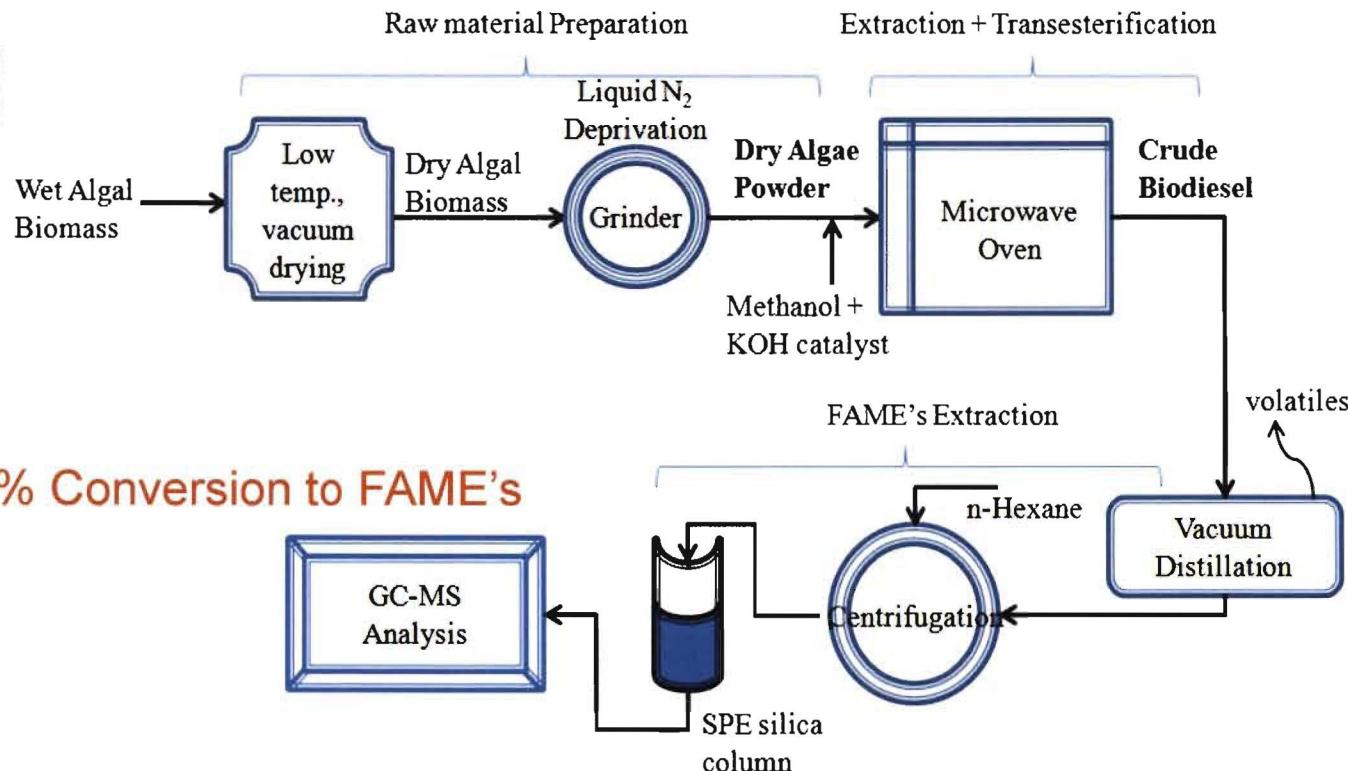


## FAME Purification Comparison

| BIODIESEL PROCESS COMPARISON CHART |           |                     |                       |            |
|------------------------------------|-----------|---------------------|-----------------------|------------|
|                                    | Units     | Catilin Pilot Plant | Commercial Test Run   | ASTM Specs |
| Feedstock                          |           | Soy                 | Mix Corn, Tallow, Soy |            |
| FFA                                | %         | <0.05               | >0.60                 |            |
| Post Treat                         |           | Dry Wash            | WFE                   |            |
| Conversion                         | %         | 99.2                | 99.9                  |            |
| Free Glycerin                      | %wt       | 0.004               | 0.004                 | <0.02      |
| M bound Glycerin                   | %wt       | 0.15                | 0.07                  | N/A        |
| D bound Glycerin                   | %wt       | 0.03                | 0                     | N/A        |
| T bound Glycerin                   | %wt       | 0.003               | 0                     | N/A        |
| Total Glycerin                     | %wt       | 0.187               | 0.074                 | <0.24      |
| Monoglyceride                      | %wt       | 0.58                | 0.27                  | N/A        |
| Diglyceride                        | %wt       | 0.20                | 0.00                  | N/A        |
| Triglyceride                       | %wt       | 0.03                | 0.00                  | N/A        |
| Acid Number                        | mg KOH/gr | 0.43                | 0.23                  | <0.5       |
| Moisture                           | %vol      | ND                  | ND                    | <0.05      |
| Calcium                            | ppm       | <1                  | 1.2                   | <5         |
| FLASH POINT                        | C         | 100                 | >150                  | >130       |
| Methanol                           | %wt       | 0.18                | <0.01                 | <0.2       |
| Cold Soak Test                     | sec       | 100                 | 60-90                 | 360        |



# Microwave Transesterification of Dry Algae



FAME: Fatty acid methyl ester ; SPE: Solid phase extraction

Patil, P.D., et al. "Optimization of microwave transesterification of dry algal biomass using RSM." *Bioresour. Technol.* accepted (2010)

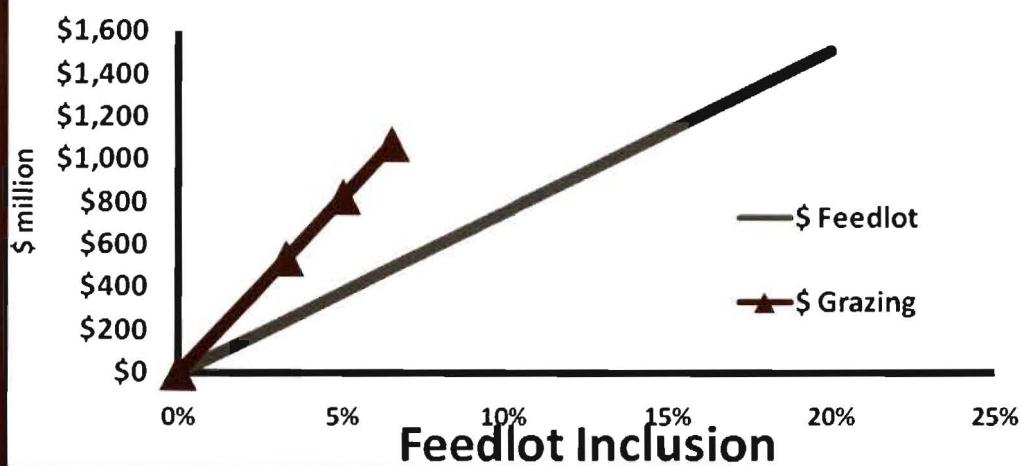


# Animal and Mari-culture Industry



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

## Utilization of Lipid Extracted Algae by the Beef Industry

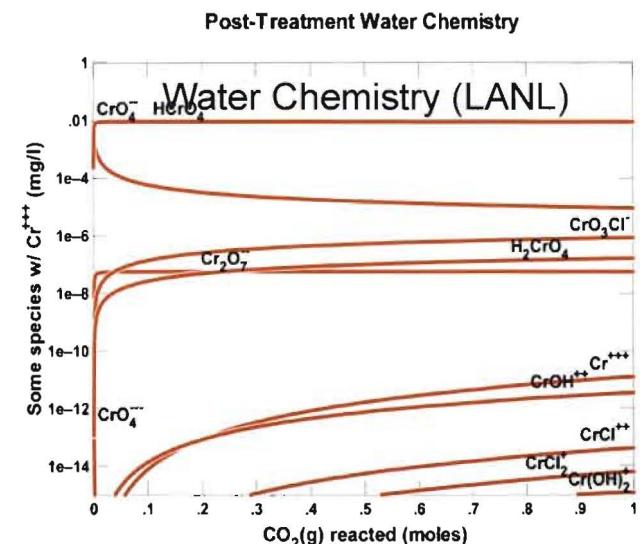
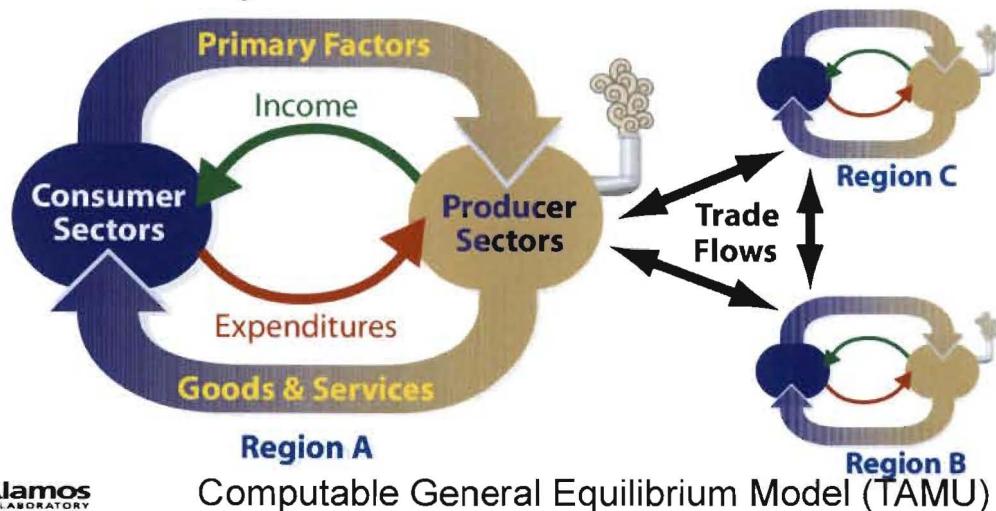


# Sustainability

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

**Economic analysis** • Economic models • Global analysis • LCA and Process Analysis

**Resource Management** • CO<sub>2</sub> management • Hydrology/water management



# 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/m<sup>2</sup>/day biomass yield (open system)

5g 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

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