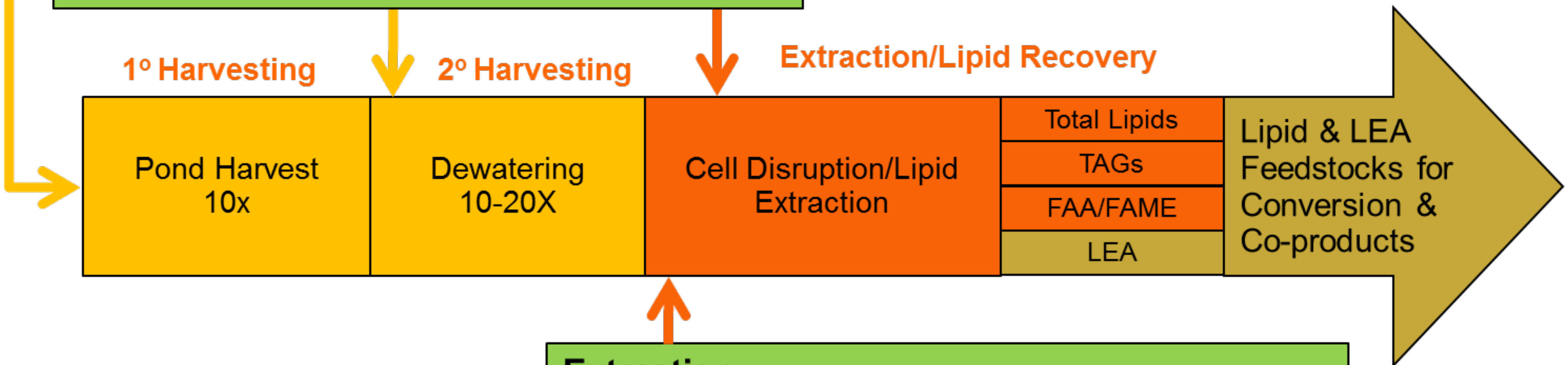
Harvesting & Extraction, Agricultural Co-products and Fuel Conversion Technical Accomplishments, Progress and Results

Presented by Kimberly Ogden, NAABB Engineering Director

Harvesting & Extraction Task Framework

Harvesting

- Chemical flocculation processes
- Electrolytic processes (field test scale-up)
- Membrane processes (field test scale-up)
- Acoustic focusing process (field test scale-up)

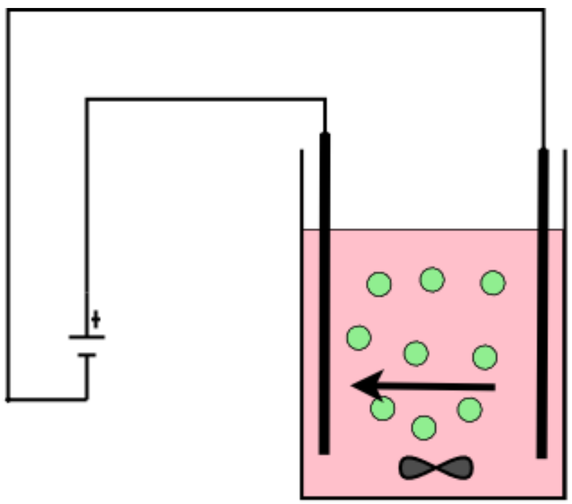


Extraction

- Amphiphilic solvent process
- Acoustic process
- Cavitation/Separation
- Mesoporous extraction FFA
- Wet Solvent Extraction (Valicor -Toll Processing)

Harvesting

- **Current bottlenecks to cost effective production of biofuels from algae – traditional is centrifuge**
- **Need to concentrate from 1 g/L to 40 or 100 g/L prior to extraction**



Electrocoagulation

Filtration

Acoustic Focusing

Harvesting Technology Comparison

Table 1 Baseline Feasibility Assessment of Harvesting-Extraction Technologies						
Technology	Energy Input (kWh/kg)	Chemical Cost (USD/Kg)	Electricity Cost (USD/kg)	OPEX (USD/Kg)	OPEX (USD/Gal)	PEL
BASELINE HARVESTING TECHNOLOGIES						
Centrifuge Baseline	3.300	0.000	0.264	0.264	1.799	56.978
Dissolved Air Floatation	0.250	0.008	0.020	0.028	0.191	4.317
Spiral Plate Separation	1.418	0.000	0.113	0.113	0.773	24.475
NAABB Harvesting Technologies						
Chitosan Flocculation	0.005	0.055	0.000	0.055	0.377	0.093
AlCl3 Flocculation	0.120	0.046	0.010	0.056	0.380	2.072
Electrolytic Harvesting	0.039	0.004	0.003	0.007	0.049	0.673
Membrane Filtration	0.046	0.000	0.004	0.004	0.025	0.789
Ultrasonic Harvesting	0.078	0.000	0.006	0.006	0.043	1.347
BASELINE EXTRACTION TECHNOLOGIES						
Pulsed Electric Field	11.520	0.000	0.922	0.922	6.280	198.906
Wet Hexane Extraction	0.110	0.001	0.009	0.010	0.068	1.904
NAABB Extraction Technologies						
Solvent Phase Algal Migration	1.648	0.947	0.132	1.079	7.352	28.446
Ultrasonic Extraction	0.384	0.000	0.031	0.031	0.209	6.630
Nanoparticle Mesoporous	0.008	54.355	0.001	54.356	370.363	0.137
Supercritical	1.174	0.000	0.094	0.094	0.640	20.271

Technologies for M1: Demonstrate 100L/hr

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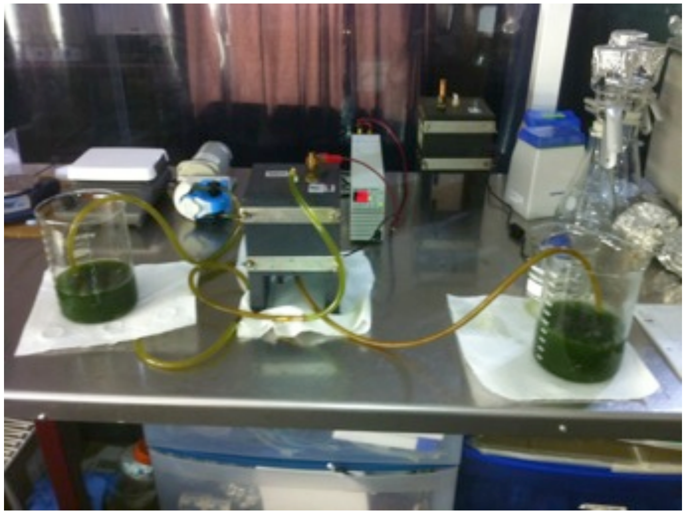
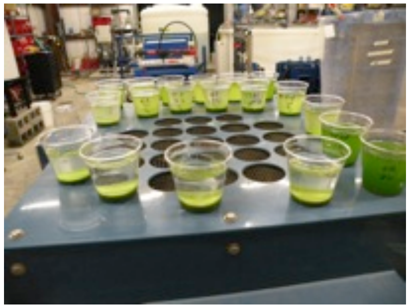
Electrolytic Separation

- Reactive metallic electrodes to produce positively charged ions that induce coagulation of the negatively charged microalgae
- Pilot Test July 2012, Pecos Texas
- Final Solids – 8%
- Energy - 0.04 kW/m^3
- Loading 270 m^3/kg hr





Comparison to base case of Centrifugation

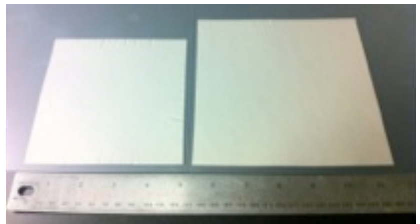
Basis - Biomass Productivity of 316,831 Tons/Year

	Centrifuge[1]	Electrocoagulation[2]
Capital Costs		
Number of Units	2,231	620
Capital Cost	$613,525,000	$403,350,000
Annual Operating Costs		
Electricity Cost (from model)	$354,000	$329,000
Labor Cost (from model)	$90,000,000	$13,000,000
Maintenance	$25,000,000	$2,800,000
TOTAL OPERATING	$115,400,000	$16,100,000

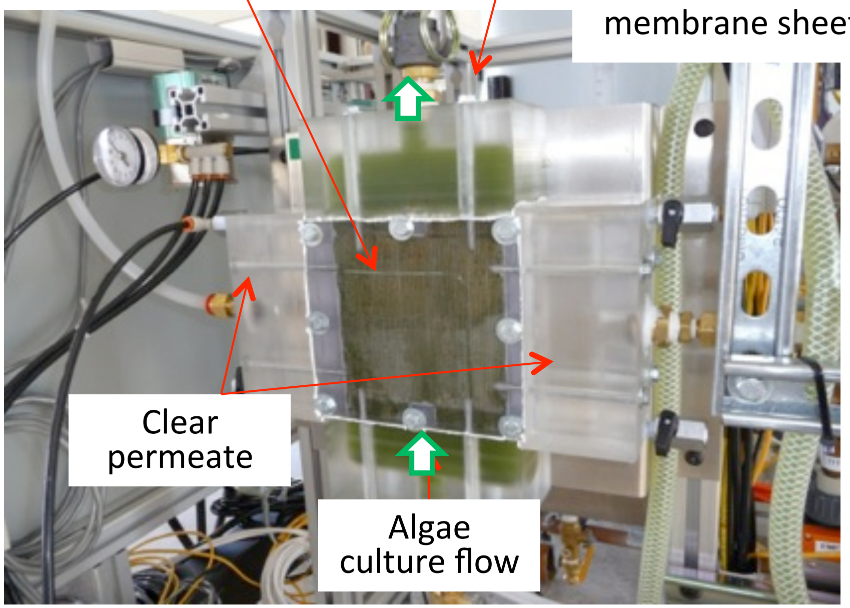
Filtration

- **Developed thin porous Ni alloy metal sheet membranes**
- **Field tests using mobile unit performed at Pecos, TX**

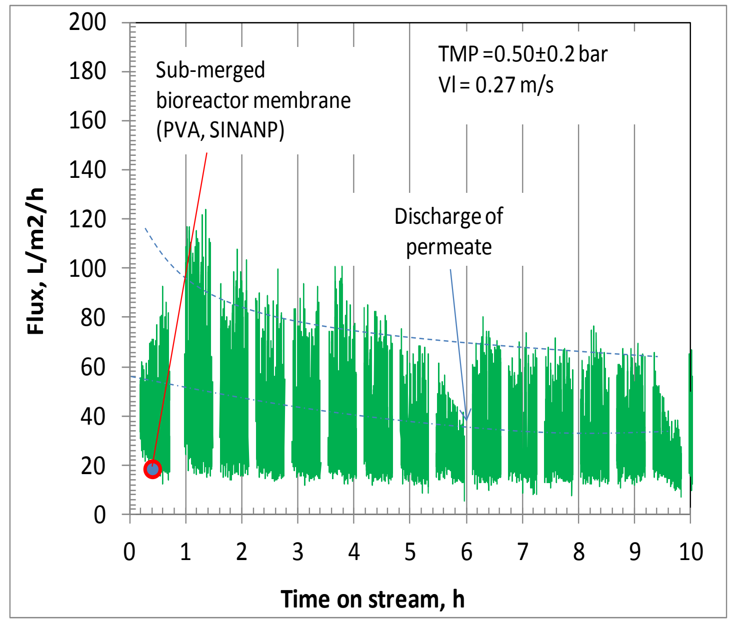
Online observation of the membrane surface



Membrane module assembled from 18 of 12 cm x 12cm membrane sheets



Filtration was conducted at relatively low liquid flow velocity with liquid/bubble slug flow

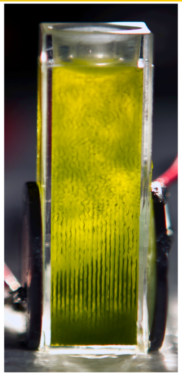


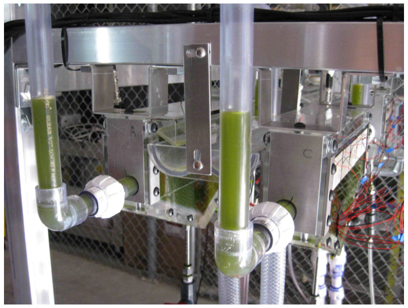
Donald Danforth Plant Science Center · Discover · Enlighten · Share · Nourish
Los Alamos National Laboratory EST. 1943
Pacific Northwest National Laboratory · Proudly Operated by Battelle Since 1965
U.S. Department of Energy

Ultrasonic Harvesting

- **Sound waves aggregate algae**
- ***Advantages*:**
  - No moving parts; No chemical additives
  - Harvested cells are still viable
  - Rapid effect—within 1 minute
  - 100X concentration effect in a single pass
  - Low energy input: 0.01-0.04 kWhr/m^3
  - Low cost: 1-4 cents per gal lipid
- ***Pilot Test* September 2012*:***
  - *N. oculata* from Solix Biosystems
- ***Scaled-up Harvester:***
  - 45-225L/hr using 9 modules
  - Scaled harvester module delivered energy to the liquid layer 100-fold more effectively than laboratory-scale unit

Concentration lines of *N. salina* in a laboratory scale harvester.





Scaled up harvester

Large scale concentration

Wet Hexane Extraction

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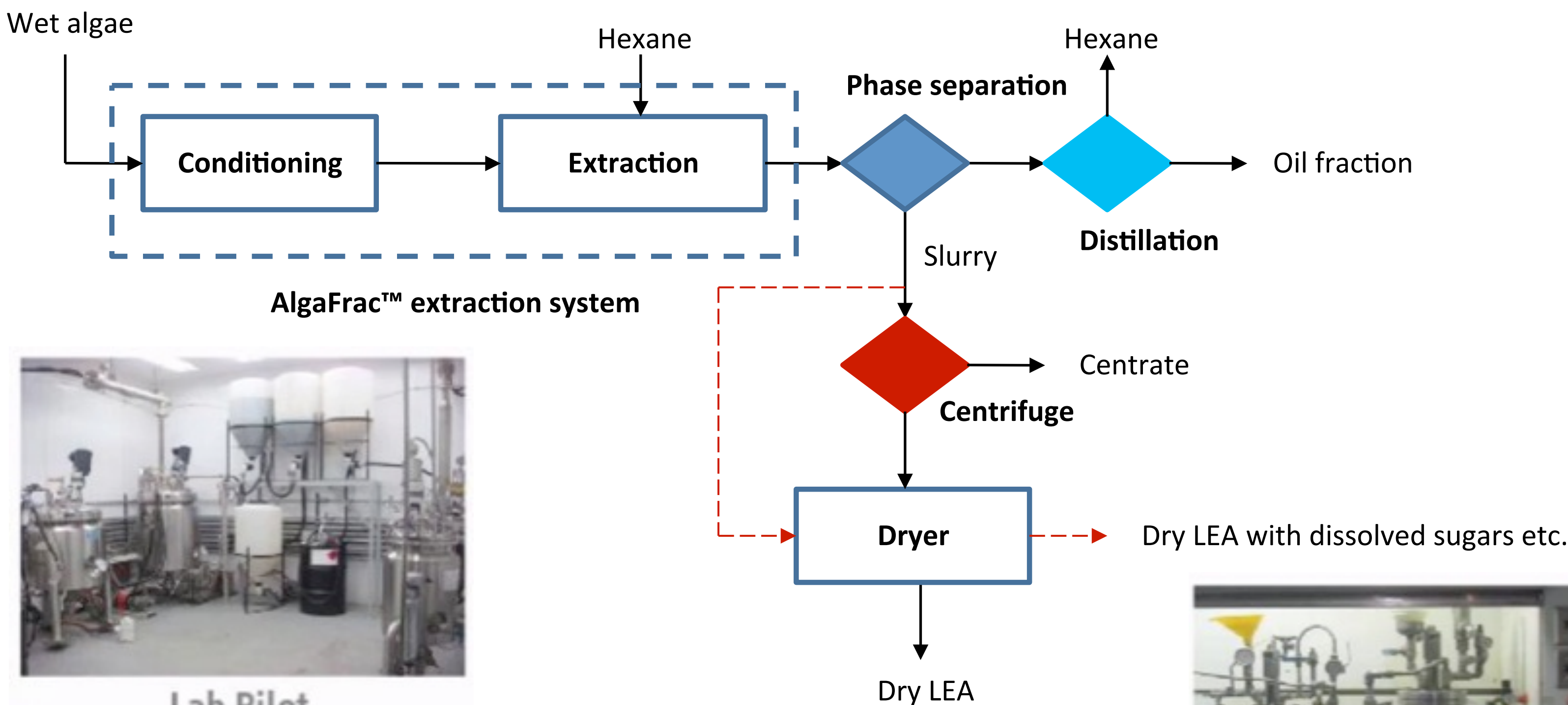
Process Schematic (Gen 1)



Lab Pilot

Bench Scale

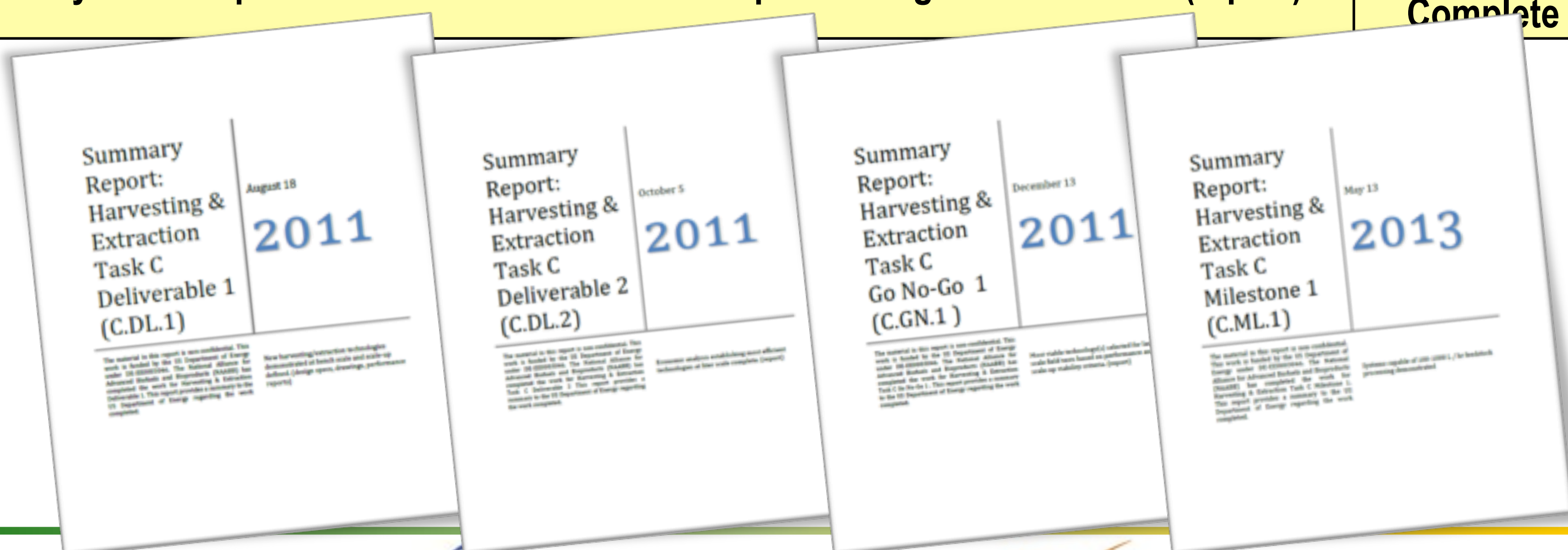
Mass Balance for *Nannochloropsis* Extraction

Nannochloropsis 1							
Date of extraction: 7/23/2012					**Extraction**		
	Algae slurry					**Oil**	
						2,015	g
Paste	**140.0**	**lb**	**Pretreatment**			**32.4%**	
AFDW content	9.8	%					
Dry wt	**6,223**	**g**					
In	**6.2**	kg			LEA - Wet	142.5	lb
Out	**6.4**	kg			Dry solids content	6.9%	%
Mass balance closure	**103.5**	%			**LEA - Dry**	**4.4**	kg

	Oil yield, wt% AFDW
Nannochloropsis 1	32.4
Nannochloropsis 2	34.5
Nannochloropsis 3	30.9
Average	**32.6**
Std deviation	**1.8**

Harvesting/Extraction Milestones and Deliverables

Milestones (M), Decision Points (GN) and Deliverables (DL)	Time (mo) Status
C.DL.1: New harvesting/extraction technologies demonstrated at bench scale and scale-up defined. (design specs, drawings performance reports)	15 Complete
C.DL.2: Economic analysis establishing most efficient technologies at liter scale complete. (report)	18 Complete
C.GN.1: (Go/No Go) Most viable technology(s) selected for large-scale field tests based on performance and scale-up viability criteria (report)	18 Complete
C.ML.1: Systems capable of 100-1000L/hr feedstock processing demonstrated. (report)	36 Complete

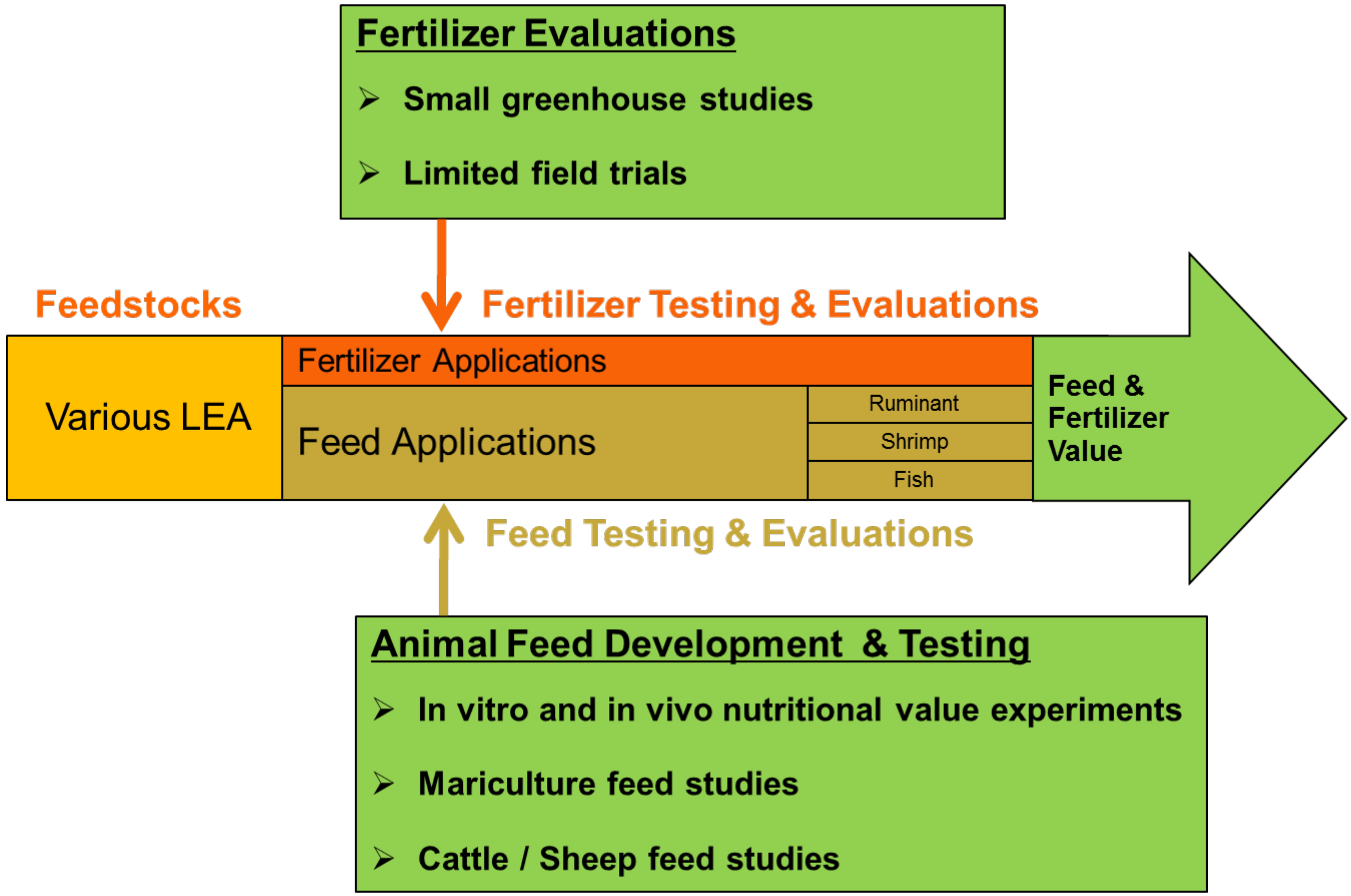


Harvesting & Extraction Synopsis

Impact

- **Harvesting and Extraction** can make up to 50% of crude oil cost
- **Started with 9 technologies**; after 18 months down selected to Harvesting technologies and 1 extraction technology
- **Conducted field tests** with target of 100 L/h processing with new low energy technologies (Electrocoagulation, Membrane Filtration, Acoustic Focusing)

Agricultural Co-products Task Framework



Feeding Results

Type of Animal Tested	Performance	Digestibility	Value
Ruminants Lambs, Cattle* *Biomass provided by DARPA (GA)	Palatable Growth, histology and blood metabolites similar to soybean -lambs	Supplementation of LEA does not impair fiber digestion Similar to cottonseed and soybean meal	Value of LEA in relation to soybean meal is ~ $160 US
Nonruminants Pigs	Reduction in growth Blood not affected		
Aquaculture Red drum, Shrimp	LEA is a suitable replacement for traditional protein feeds for fish and shrimp production		Excellent but minerals of concern

Chemical/Nutritional Characterization of LEA

	Soybean Meal	Chlorella Pecos (open ponds)	Chlorella Pecos (open ponds)	Nannochloropsis Solix (photobioreactor)
Extraction Method	Solvent	Valicor – high temperature	Valicor– low temperature	Solix Solvent - hexane
Nutrient Composition, % DM				
Ash	6.3	43.4	39.2	4.7
Crude Protein	42.3	20.3	22.0	34.3
Neutral Detergent Fiber	14.9	22.1	24.3	36.7
Acid Detergent Fiber	---	10.5	13.2	23.0
Lipid (Folch method)	2.3	5.2	5.4	11.1
Calcium, %	0.4	6.4	5.6	0.3
Phosphorus, %	0.7	0.4	0.4	1.1
Sodium, %	0.04	5.5	5.7	1.4
Chloride, %	0	3.4	5.0	1.1
Aluminum, ppm	---	3590.0	4170.0	48.4
Iron, ppm	185.0	5110.0	5600.0	435.0

Ag Co-products Milestones and Deliverables

Milestones (M), Decision Points (GN) and Deliverables (DL)	Time (mo) Status
E.1.ML.1: Feed Value for LEA Determined	24 Complete
E.2.DL.1: Preliminary cost analysis, bench scale rate data, and yield information obtained for production chemicals	24 Complete
E.1.DL.1: Best performing feed formulations determined(report)	36 Complete

Agricultural Co-products Synopsis

Impact

- **LEA varied in quality** in terms of ash, protein and residual lipids based on strain, cultivation site and processing methods
- **Generally LEA work well as feed supplement** by inclusion studies for all animals tested (cattle, sheep) and (shrimp, fish) but not swine
- **LEA also worked as a fertilizer/soil amendment** although values for this application were extremely low ($30/ton)
- **Values for the LEA** as a feed supplement for animals ($160/ton) and mariculture ($200/ton) generally do not provide a high enough value to offset algal oil production costs

Fuel Conversion Task Framework

NAABB National Alliance For Advanced Biofuels and Bio-products

Lipid Conversion to Fuels

- **Processes to produce Biodiesel fuels (FAMEs)**
  - Solid Acid Catalyzed
  - Sub-Supercritical
- **Processes to produce hydrocarbon fuels**
  - Hydrogenation
  - Decarboxylation

Detailed Characterization

- **Chemical & physical characterization of feedstock (lipid/LEA)**
- **Chemical & physical characterization of fuel products**
- **Quality/Performance evaluations of fuel products**

Feedstocks

- Various Lipid Extracts
- Algal Biomass
  - Whole Biomass
  - Various LEA
  - Macroalgae

Lipid Conversions Processes

- Biodiesel
- Hydrocarbon Fuels
- Methane/Power
- Ethanol
- Organic Acids/Gasoline
- Bioplastics
- Refinery Feedstock

Product / Process Characterization & Evaluations

Biomass Conversions Processes

Biomass/LEA Conversion to Fuels & Chemicals

- **Hydrothermal gasification to methane for power**
- **Hydrothermal Liquefaction and upgrading to hydrocarbon fuels**
- **Biological conversion: organic acids to gasoline, ethanol**
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Hydrocarbon Fuels

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Refinery Feedstock

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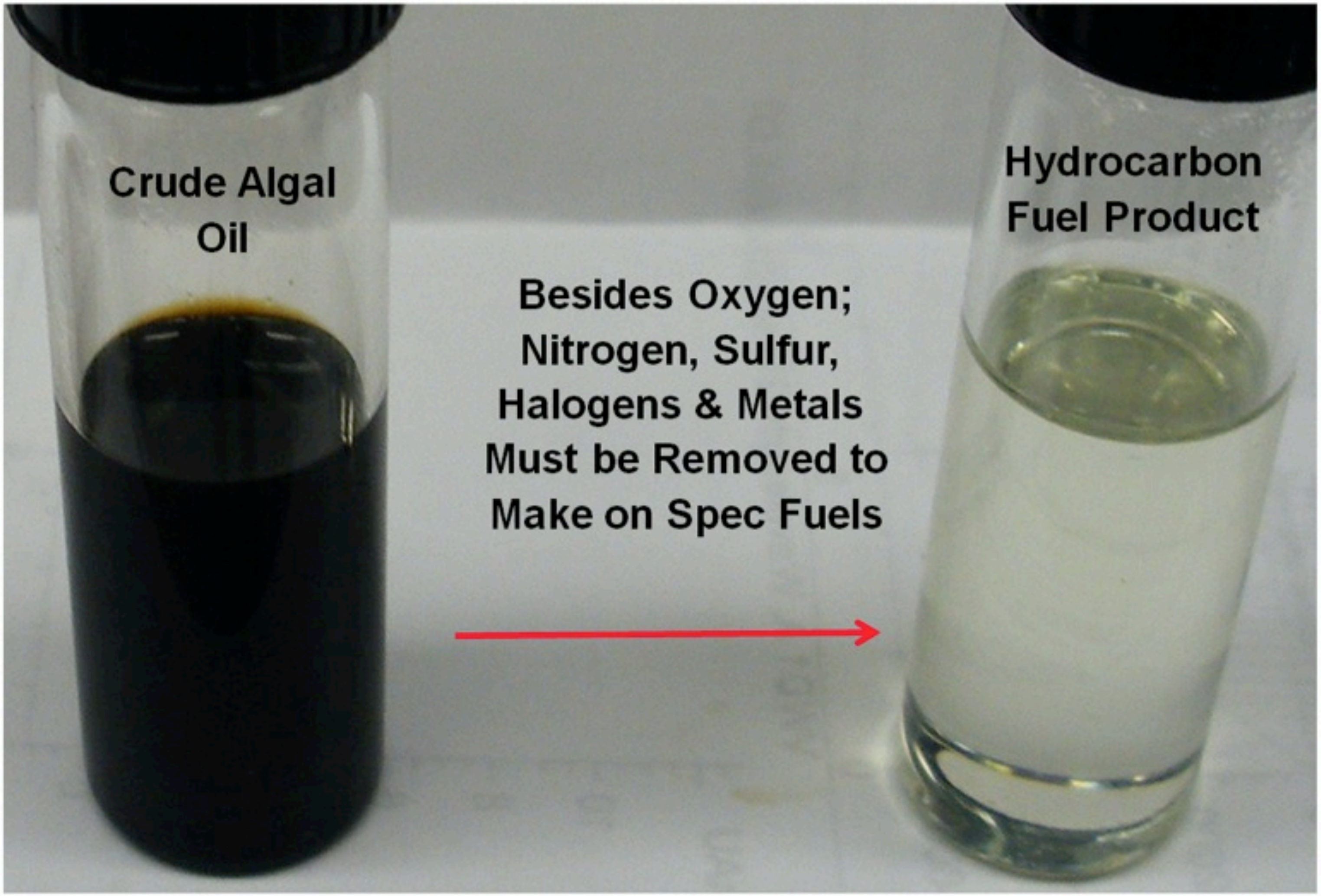
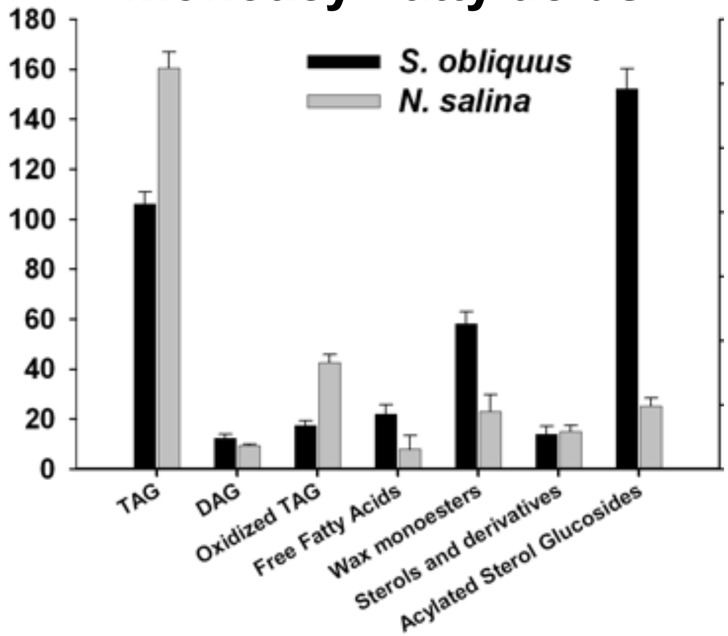
Conversion Lipid Extracts to Fuels

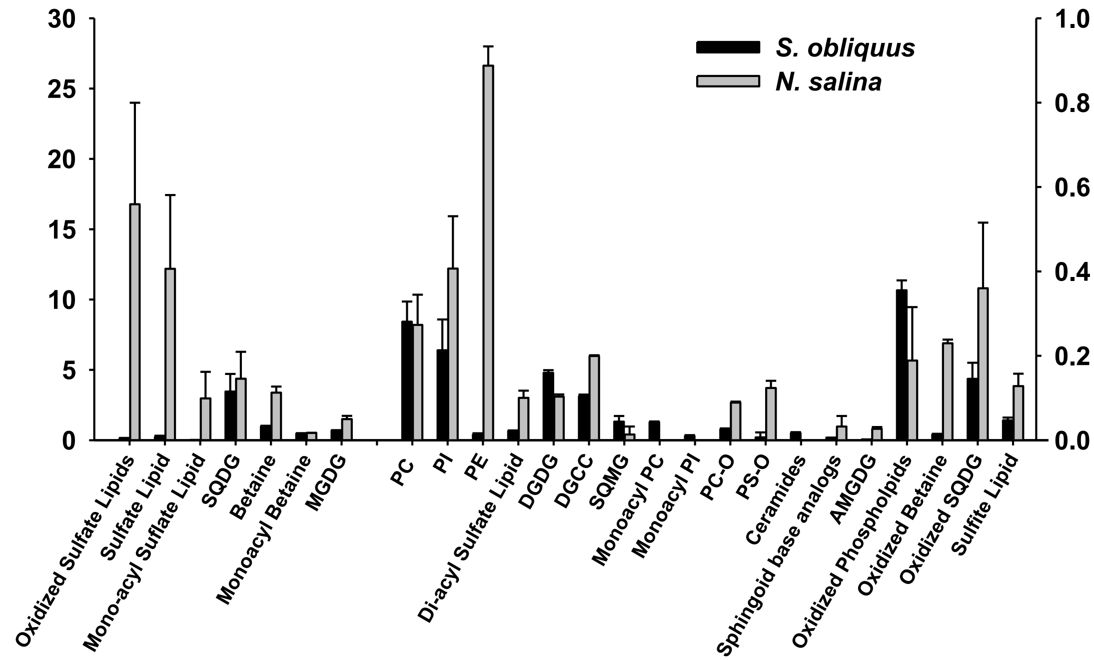


"Contaminants" for Conversion are "Nutrients" for Cultivation

Chemical/Physical Characterization of Lipids

- **FT-ICR Mass Spectrometry Analysis**
- **1000 to 1500 peaks per ionization mode (positive ion or negative ion)**
- **Detect phospho-lipids, acyl attached fatty acids, monoacyl fatty acids**





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Conversion of Lipid Extract to Biodiesel

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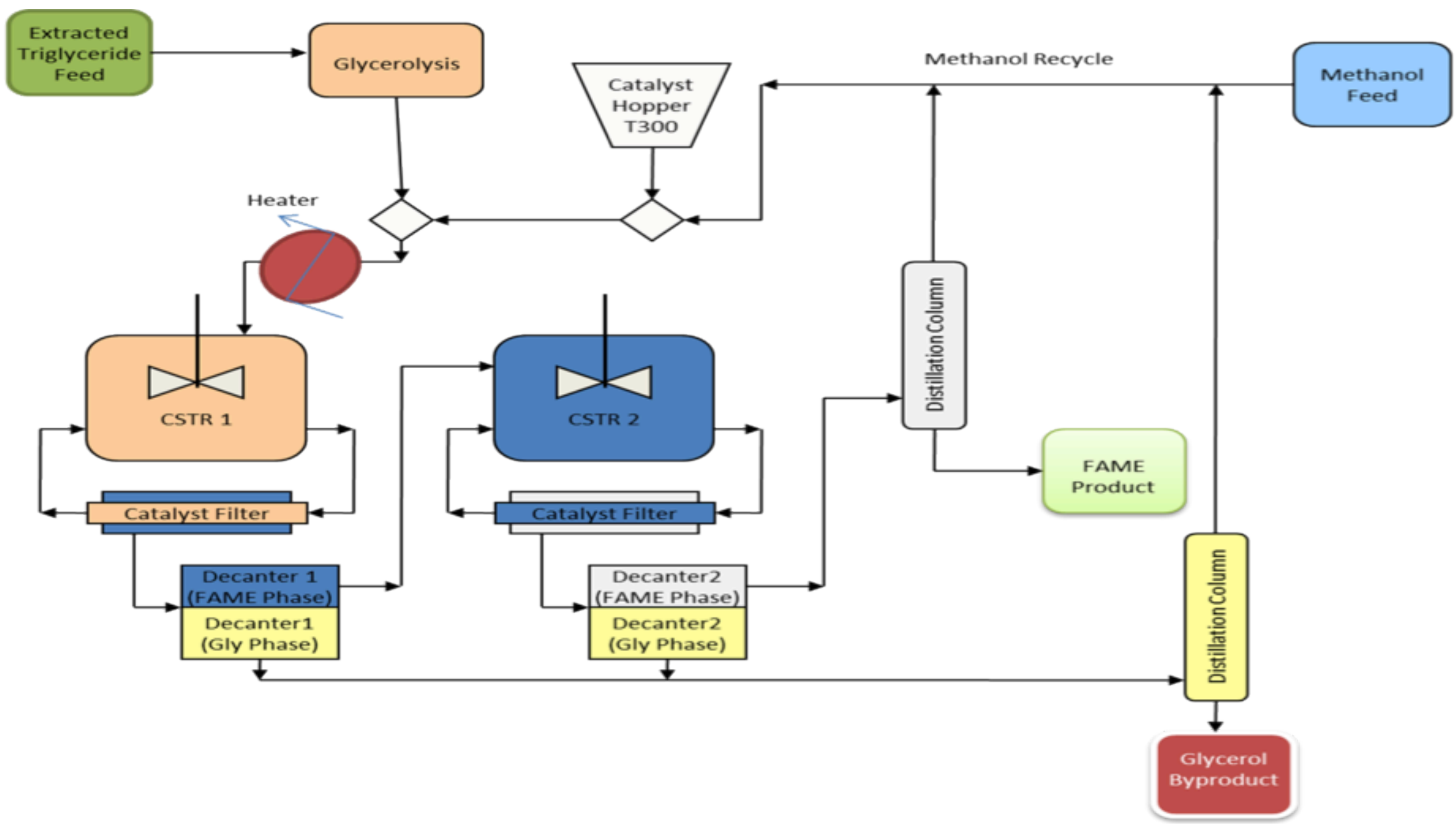
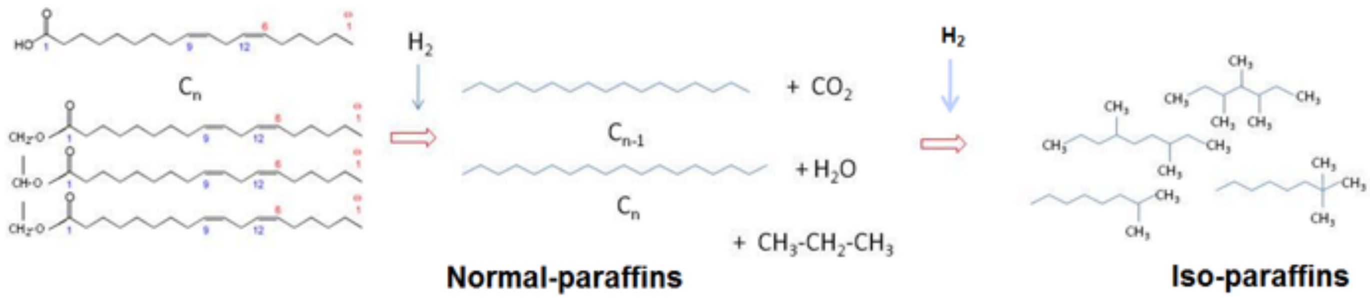


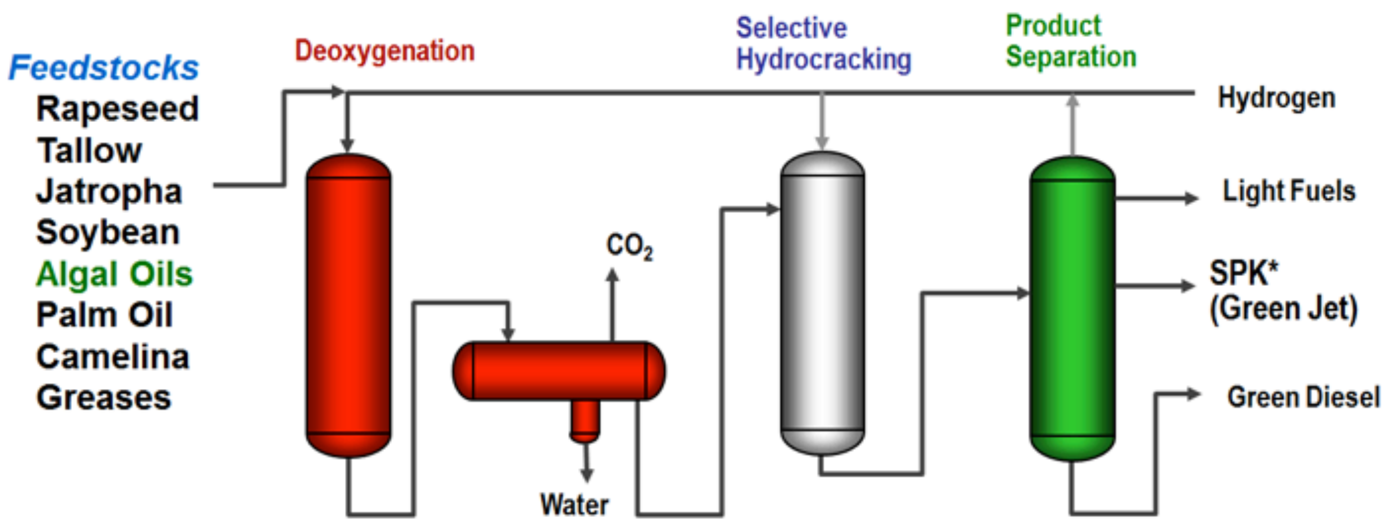
Conversion of Lipid Extract to Hydrocarbon Fuels

National Alliance For Advanced Biofuels and Bio-products

UOP's Renewable Jet Fuel & UOP/ENI Ecofining Processes

A Honeywell Company





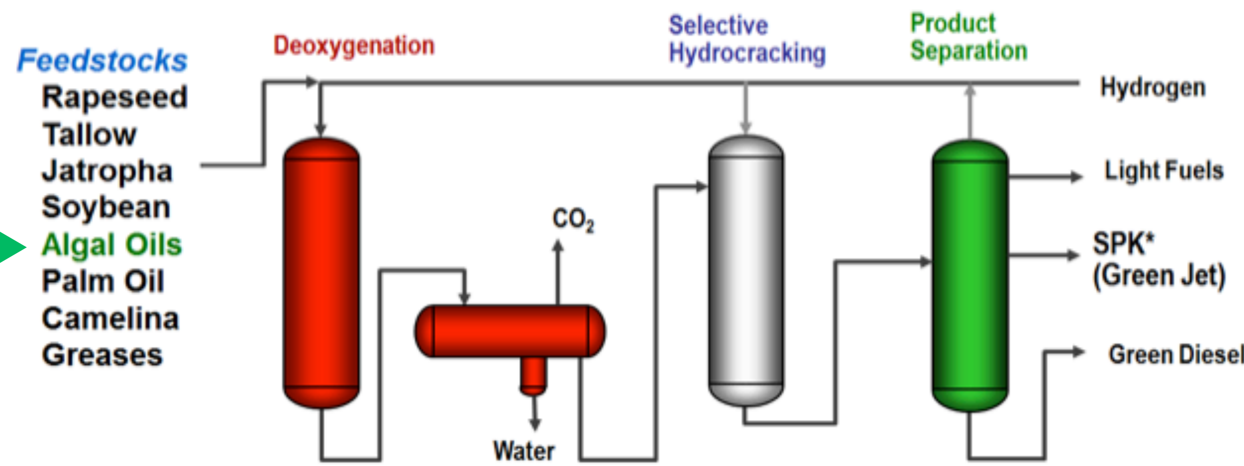
*SPK = Synthetic Paraffinic Kerosene

Feedstock Versatile Process for Green Diesel & Green Jet

Conversion of Lipid Extract to Hydrocarbon Fuels

Pretreatment Technologies to "Clean Up" Algal Lipid Extract

3 Invention Disclosures



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Chemical/Physical Characterization of Jet Fuel

Parameter	D7566 HEFA Specification	Jet Fuel from Algal FAME	Jet Fuel from Algal TAG Oil #1	Jet Fuel from Algal TAG Oil #2	Jet Fuel from Algal TAG Oil #3	Jet Fuel From Algal TAG Oil #4	Jet Fuel from Algal FAME Oil
Density (g/L)	730 - 770	755.2	753.1	754.2	756.9	749.4	767.6
Freeze point (°C) max	-47	-48.6	-62.6	-50.4	-61.8	-80	-70.6
Flash Point (°C) min	38	42.5	39.7	44	45	40.2	85.4
Distillation							
10% Recovered Temp (T10) °C max	205	156.4	160.2	151.4	150.4	152	208.2
50% Recovered Temp (T50) °C	Report	192	193.8	191.4	189	180	231.6
90% Recovered Temp (T90) °C	Report	248.8	245.6	252.4	234.8	222.2	257
Final Boiling Point (°C) max	300	279	271.8	293.2	284.2	263.6	289
T50-T10 min	15	35.6	33.6	40	38.6	28	23.4
T90-T10 min	40	92.4	85.4	101	84.4	70.2	48.8

Chemical/Physical Characterization of Algal Diesel

Parameter	F-76 Naval Distillate	ULSD Specifications	Algal Diesel From TAG Oil #1	Algal Diesel from TAG Oil #2	Algal Diesel From TAG Oil # 3	Algal Diesel From FAME Oil
Density at 15° C, g/L (max)	876	-	778.2	770	783.2	777.4
Flash Point, ° C (min)	60	52	91.2	62.7	120.9	85.2
Cetane Number (min)	42	40	92	85	106	ND
Sulfur (max %)	0.15	0.0015	0.0003	0.0001	<0.0001	0.0001
Distillation 90%Recovered, ° C (max) (min)	357	338 282	288.4	305	320	294.8
Distillation End Point, ° C, (max)	385		317.8	324.8	345.8	330.4
Cloud Point, ° C (max)	-1	By geography	-20.5	-16.2	4.4	-6.9
Pour Point, ° C (max)	-6	By geography	-24	-21	3	-12
Metals (ppm) max Calcium Lead Sodium + Potassium Vanadium	 1 0.5 1 0.5	 - - - -	 <0.009 <0.01 0.29 <0.009	 0.024 < 0.02 0.026 < 0.009	 0.17 <0.04 0.25 <0.01	 <1 <0.02 <1 <0.01

Fuel Conversion Task Framework

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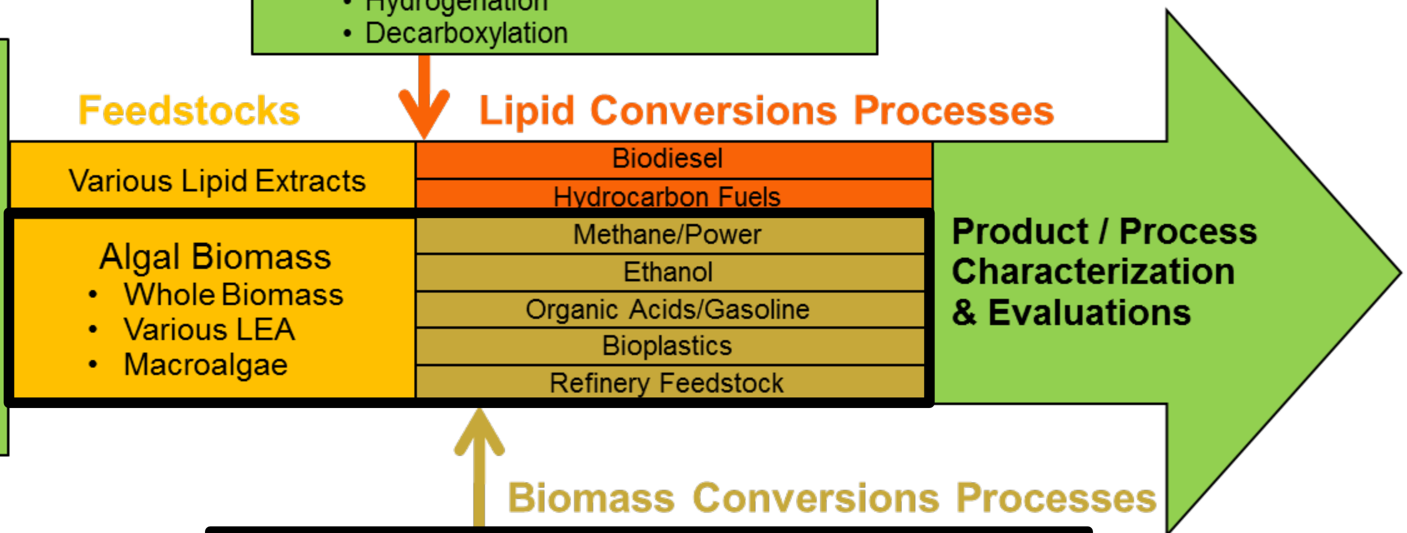

Biomass/LEA Conversion to Fuels & Chemicals

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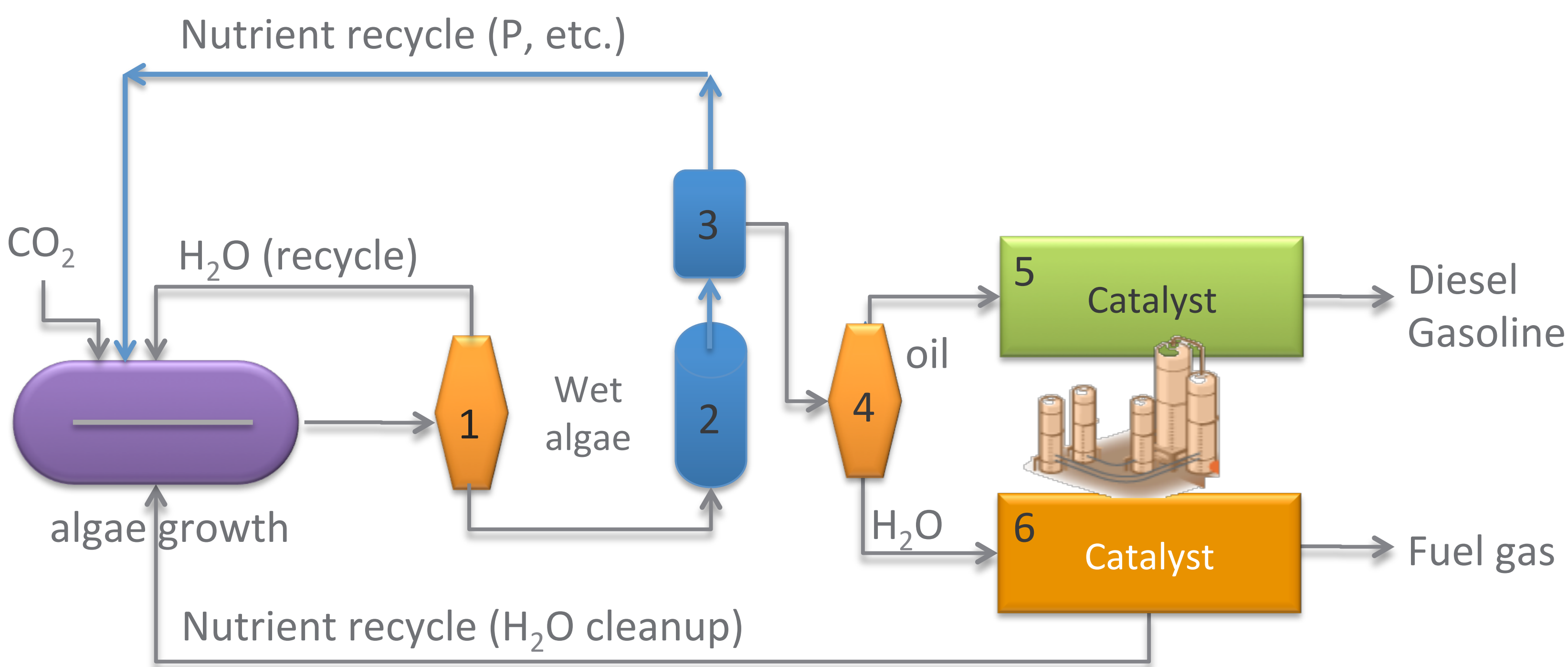
Hydrothermal Conversion of LEA and Whole Algae



1. algae de-watered from 0.6 g/l to 100 g/L
2. hydrothermal liquefaction
3. solid precipitate separation for clean bio-oil production and phosphate capture
4. oil/water phase separate
5. oil hydrotreater to produce hydrocarbons—diesel/gasoline)
6. aqueous phase carbon is catalytically converted to fuel gas and nutrients recycled (N, K, CO_2)

Hydrothermal Conversion of Whole Algae

1

100 g algae
23% ACF*
Dry basis

Hydrothermal Liquefaction
348° C
2900 psi
LHSV = 2.2 hr^{-1}
(~15 min residence time)

2

64 g bio-oil
18% ACF*
Dry basis

Hydrotreater
105-401° C
2000 psig
LHSV = 0.20 hr^{-1}
85 L/hr H_2
0.026 g H_2 consumed/ g feed

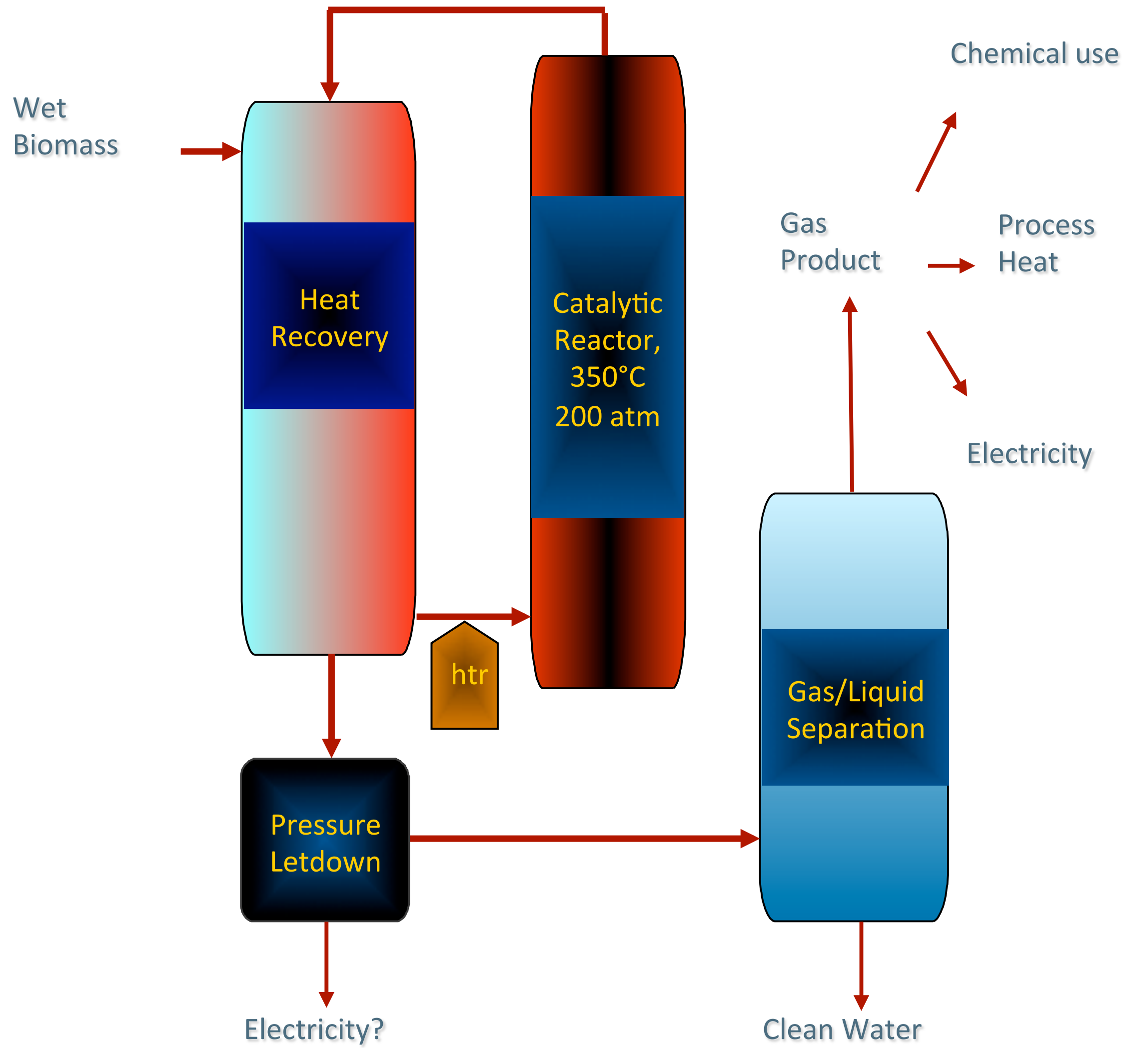
3

47 g
High value refinery feedstock oil
Dry basis

Stream Description	Ultimate Analysis					Dynamic Viscosity, mPa-s (40°C)	Density, g/mL (40°C)	Water, wt%	Acid Number, mg KOH/g
	C	H	N	O	S				
PNNL HTL Bio-oil									
HT Feed	77.6	10.6	4.0	7.2	0.3	512	0.96	11.0	56
HT Product	84.2	14.0	0.08	1.7	<0.005	4.9	0.78	0.27	0.1

Catalytic Gasification

- **Low-temperature, single-step synthetic natural gas from algae and LEA**
- **Metal catalyst**
- **High-pressure steam reforming & methanation**



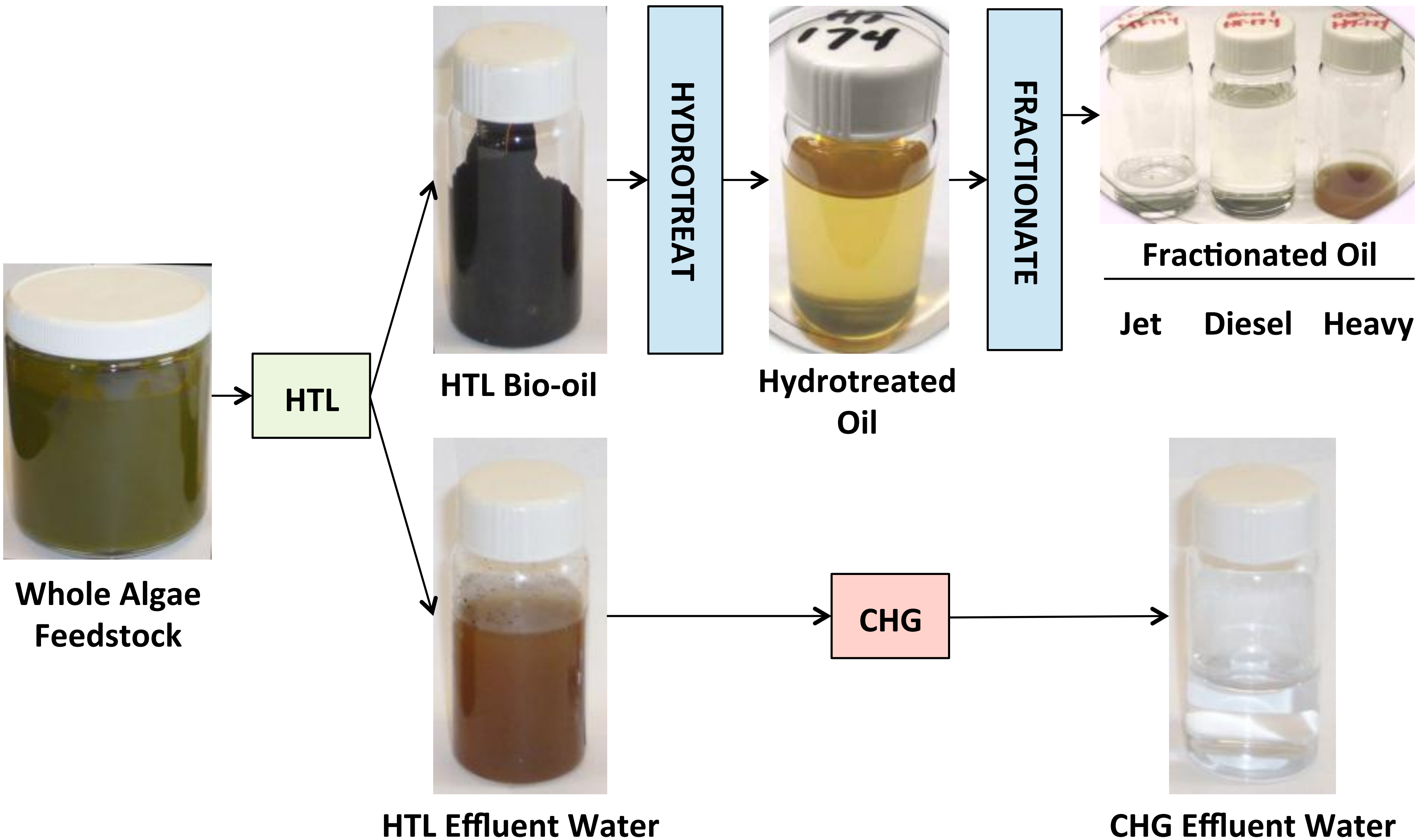
$$C_xH_yO_z + nH_2O \rightarrow aCH_4 + bCO_2$$

Equilibrium Control of Gasification

Combined HTL & CHG Conversion of Whole Algae

TEM	DATA
Lipid content of whole algae	33%
Bio-oil from HTL as % algae mass	58%
Bio-oil from HTL as % algae AFDW	64%
% of algae carbon in HTL oil	69%
Mass of organic residual in effluent water	34%
% of organic in effluent converted to CH_4	50%
Total carbon recovery as fuel (oil + CH_4)	86%

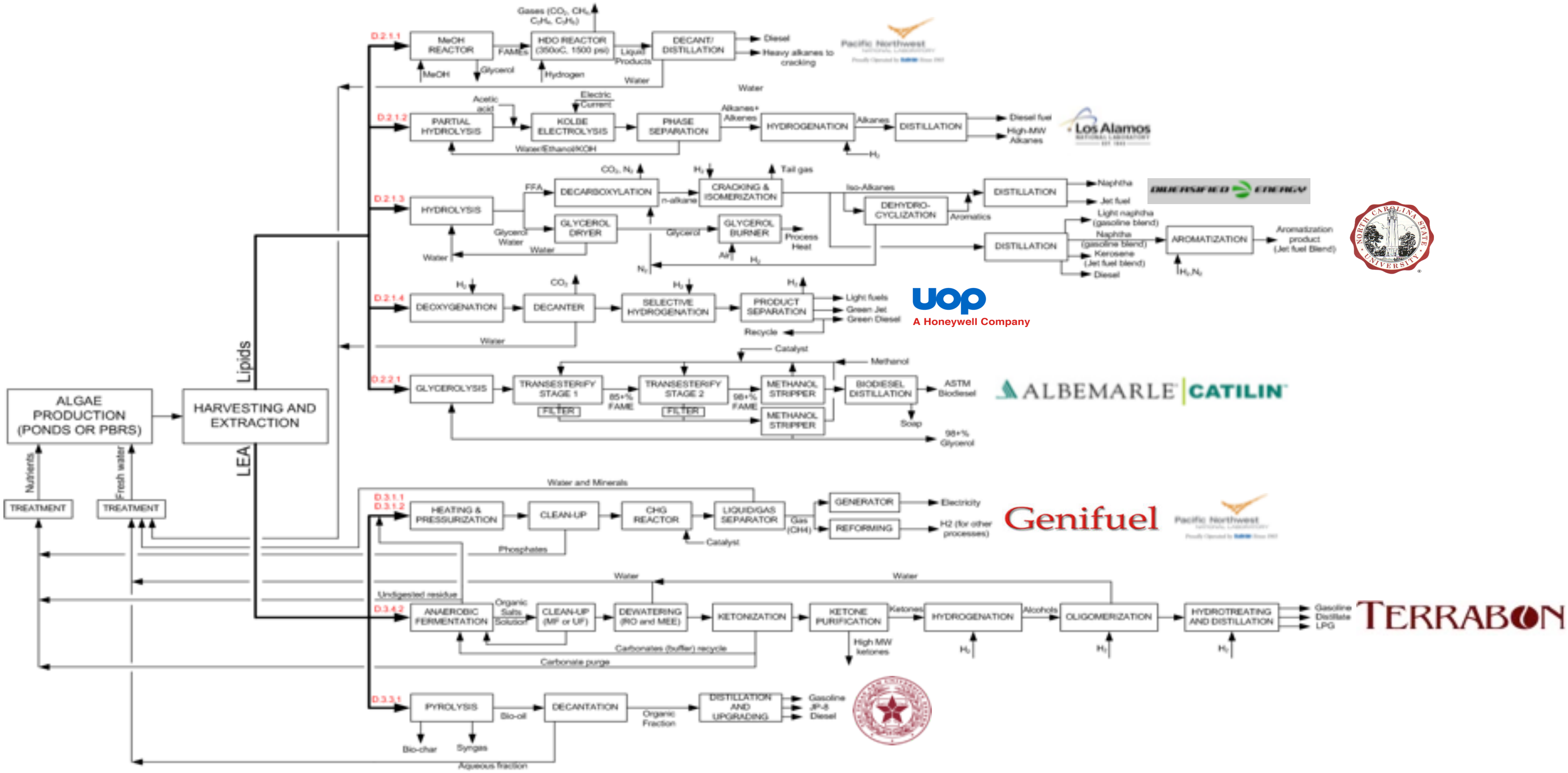
Combined HTL & CHG Conversion of Whole Algae



Chemical/Physical Characterization of Jet Fuel from HTL Conversion

Parameter	Jet A	Jet A1	Jet Fuel From HTL Algal Bio-Oil #1	Jet Fuel From HTL Algal Bio-Oil #2
Density (g/L)	775 - 840	775 - 840	786.3	780.2
Freeze point (°C) max	-40	-47	-45.8	-57
Flash Point (°C) min	38	38	61.2	59.6
Distillation				
10% Recovered Temp (T10) °C max	205	205	167.8	167
50% Recovered Temp (T50) °C	Report	Report	207.4	203.6
90% Recovered Temp (T90) °C	Report	Report	244.6	242.2
Final Boiling Point (°C) max	300	300	273.2	272

Summary of NAABB Lipid and Biomass Conversion Processes



Fuel Conversion Milestones and Deliverables

Milestones (M), Decision Points (DP) and Deliverables (DL)	Time (mo) Status
D.DL.3: Preliminary cost analysis, bench scale rate data, and yield information obtained (report)	24 Complete
D.ML.1: Select optimal conversion process for large-scale production and wide-scale use based on performance and scale-up requirements criteria (design specs, report)	24 Complete
D.DL.1: Pollutant and greenhouse gas emissions from the combustion of algae-derived biofuels characterized. (report)	30 Complete
D.DL.2: ASPEN process model of conversion technologies demonstrated. (report)	30 Complete

Fuel Conversion Synopsis

Impact

- Processed **algal biomass, lipid extracts and LEA** from >5 species using multiple technologies to finished fuel products (one-of a kind data set of data)

- **Crude lipid extracts to finished fuels** (Biodiesel and HC Fuels) 1) low carbon yield to fuels due to clean-up losses; 2) Fuel products could meet fuel specs (issues with impurities)

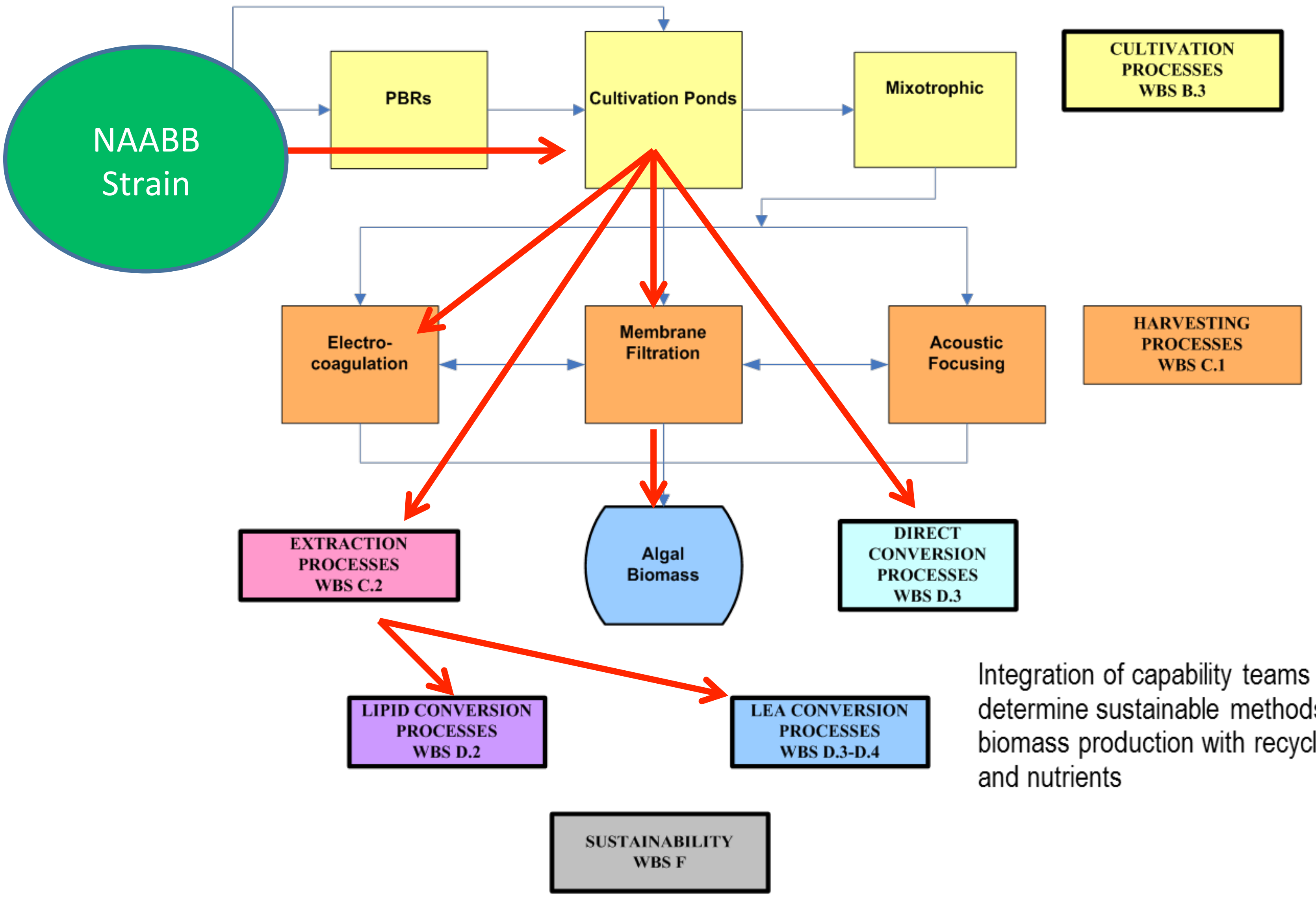
- **Demonstrated conversion of LEA** (CH_4, ethanol, organic acids)

- **Liquefaction combines extraction with conversion** and has the potential to significantly improve yields (2X) over the wet extraction baseline

Downstream Process Outcomes

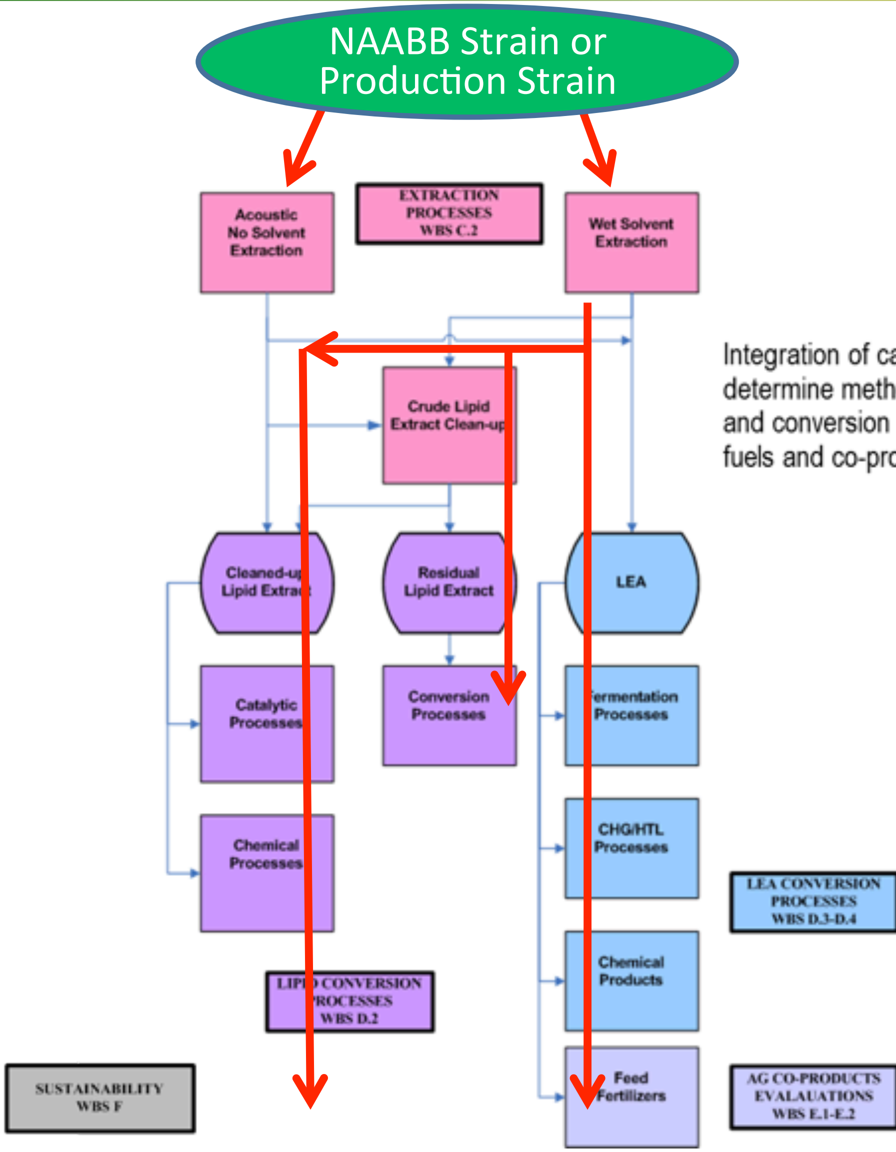
- **All Deliverables and Milestones Accomplished**
- **New Harvesting and Extraction Technologies Tested in Field**
- **Cost Analyses (CAPEX and OPEX) for all downstream processes**
- **Process Models (ASPEN) for all Conversion Processes as well as Growth Model**
- **Technology transfer activities in progress**
  - Electrolytic Harvesting
  - Acoustic Focusing
  - Membrane Filtration
  - HTL/CHG
- **Integrated Systems – Critical Success Factors**

Cultivation/Harvesting/Water & Nutrient Recycling



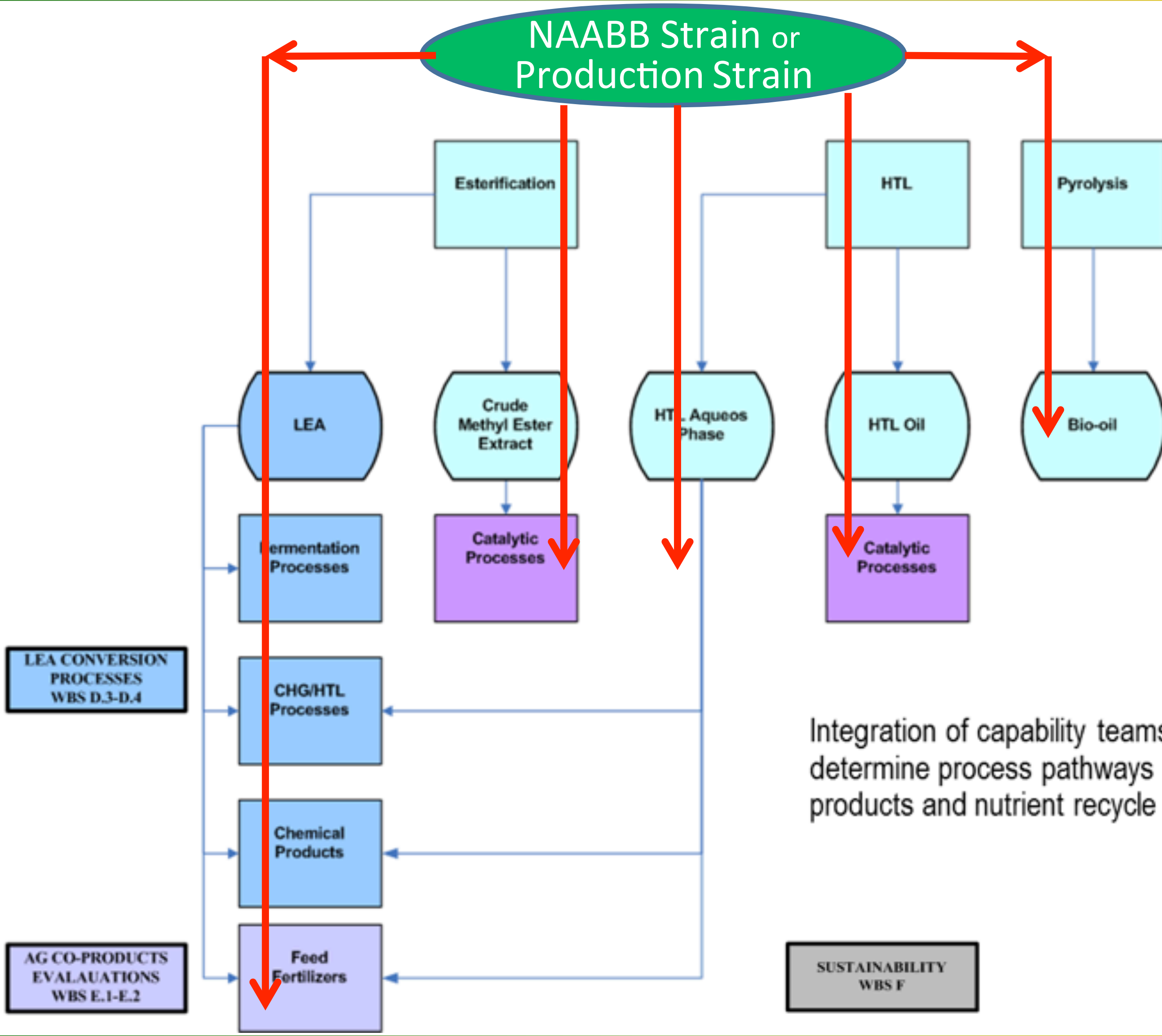
Integration of capability teams to determine sustainable methods for algal biomass production with recycle of water and nutrients

Extraction/Lipid Clean-up and Conversion



Integration of capability teams to determine methods for lipid, extraction and conversion of lipids/ LEA fractions to fuels and co-products and nutrient recycle

Direction Conversion to Fuels & Co-products



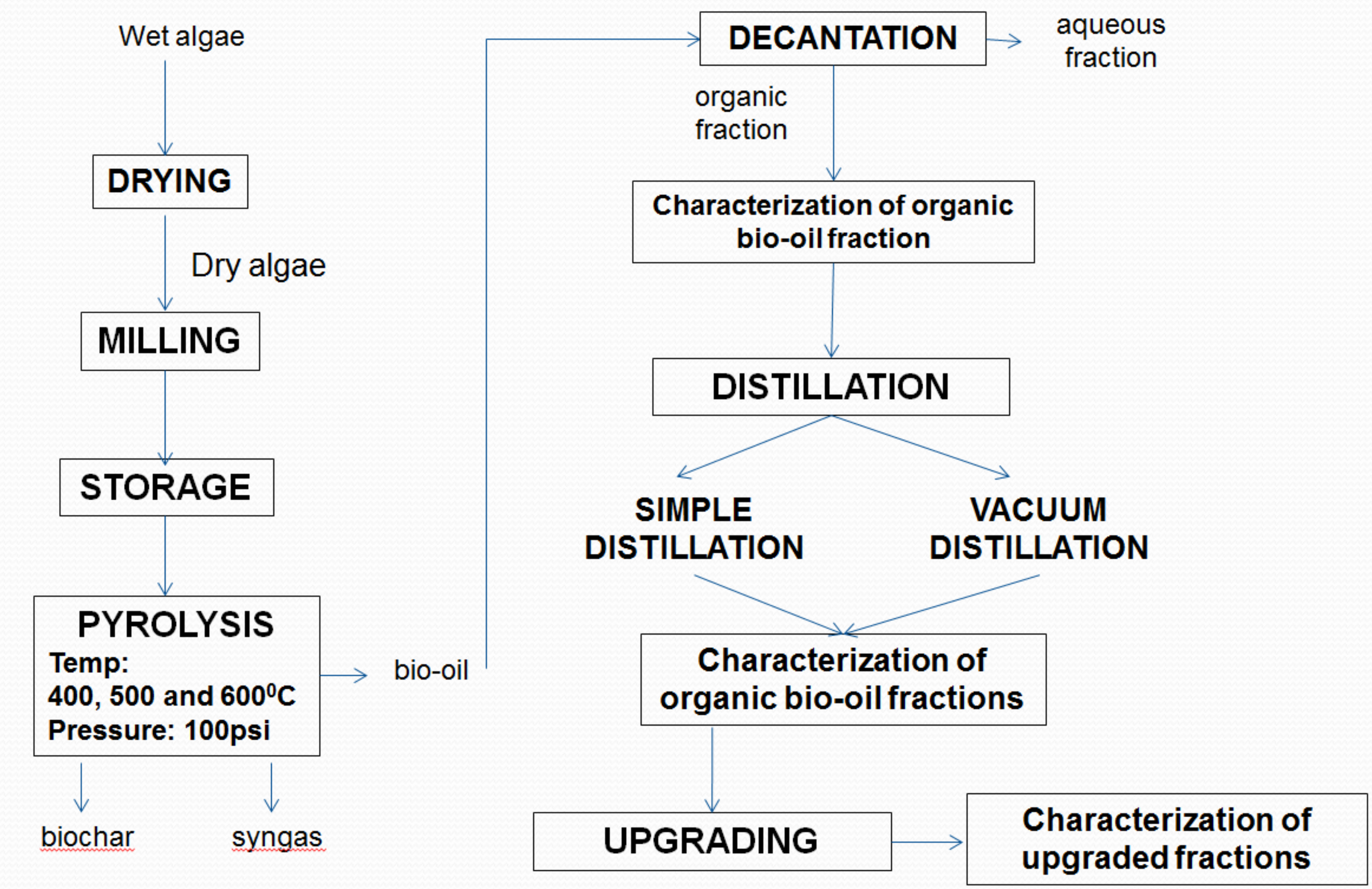
Integration of capability teams to determine process pathways for fuels, co-products and nutrient recycle

Questions?

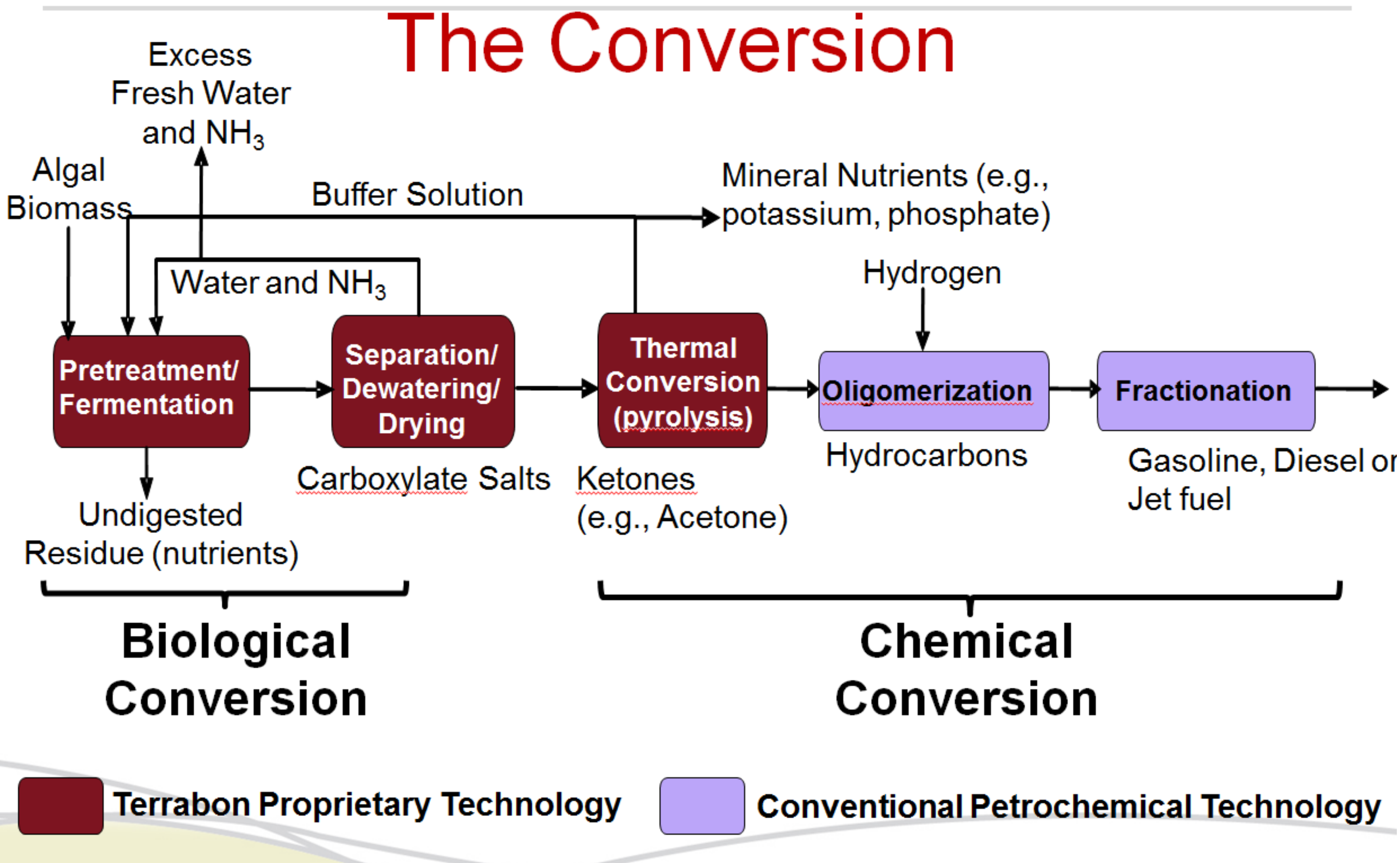
Back up Slides

Conversion of Whole Algal Biomass to Fuel via Direct Pyrolysis

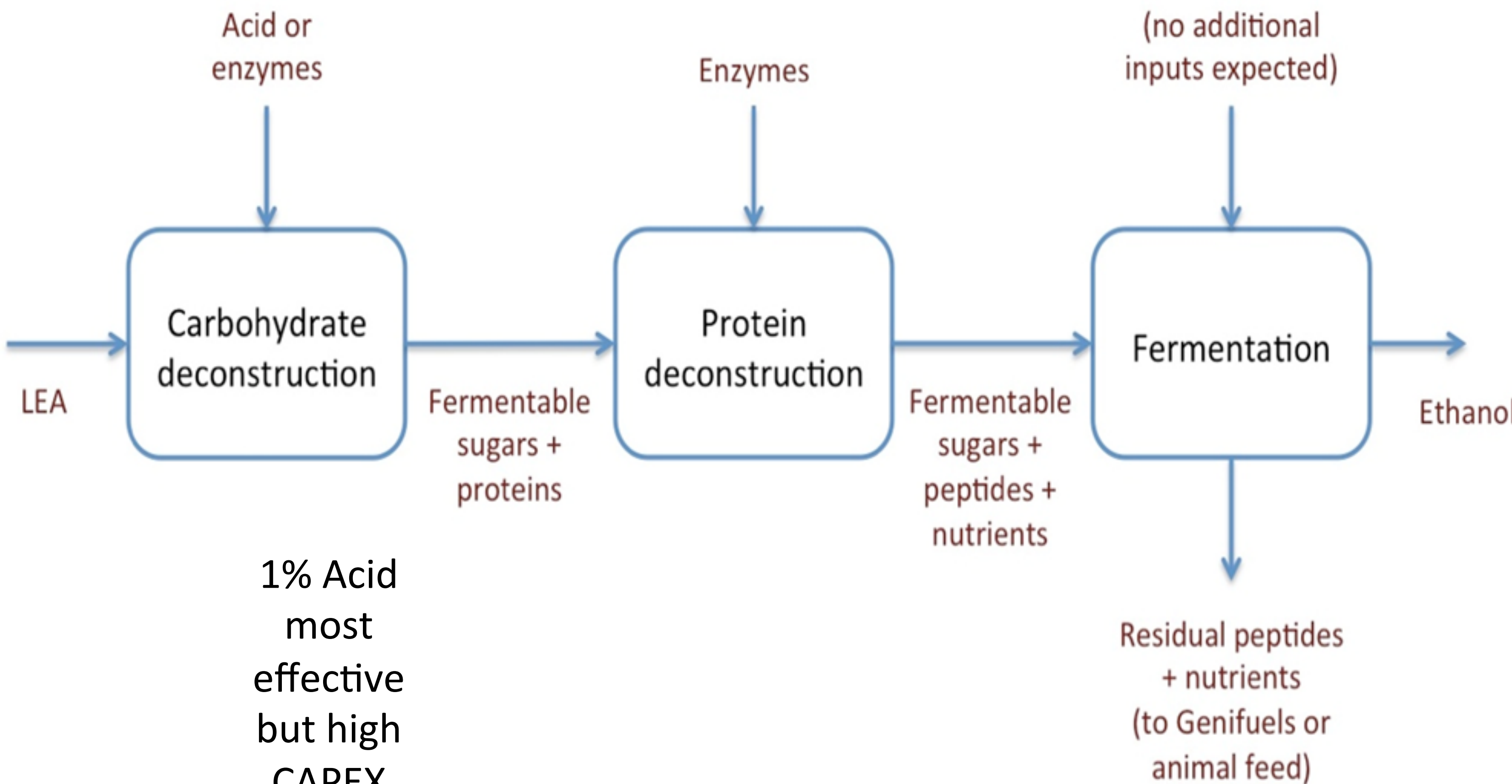
GENERAL RESEARCH ROADMAP



Conversion of LEA to Fuels via Biological and Chemical Processes



Conceptual process flow diagram



1% Acid most effective but high CAPEX