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Recent Developments in Hydrothermal Processing of Algae

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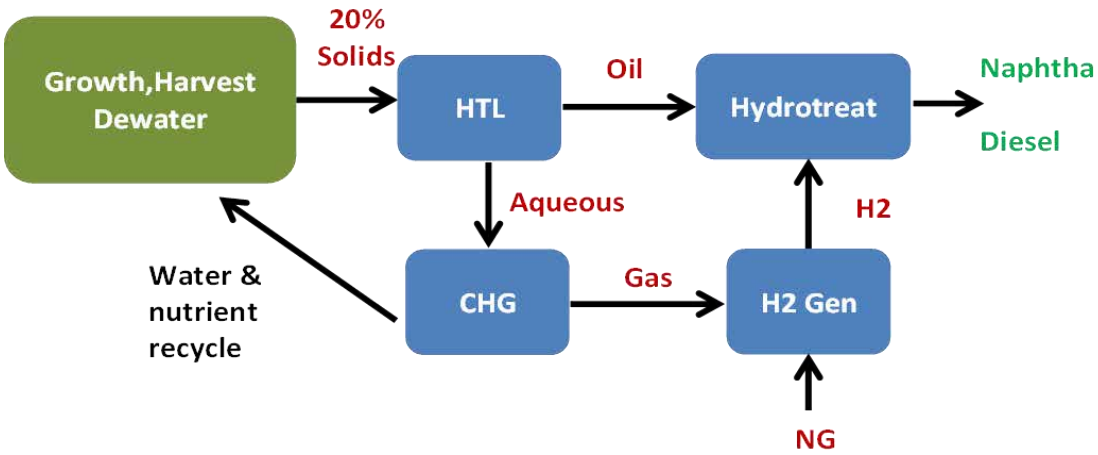
Pacific Northwest National Laboratory

Bioenergy 2016, The National Algal Biofuels Technology Review, Washington, DC, July 14, 2016

Outline

- HTL at PNNL
- Upgrading of HTL biocrude
- CHG of aqueous phase
- Preliminary TEA/LCA
- Commercialization and future work

Box Flow for Algae Application



Simplified HTL Process Flow Diagram

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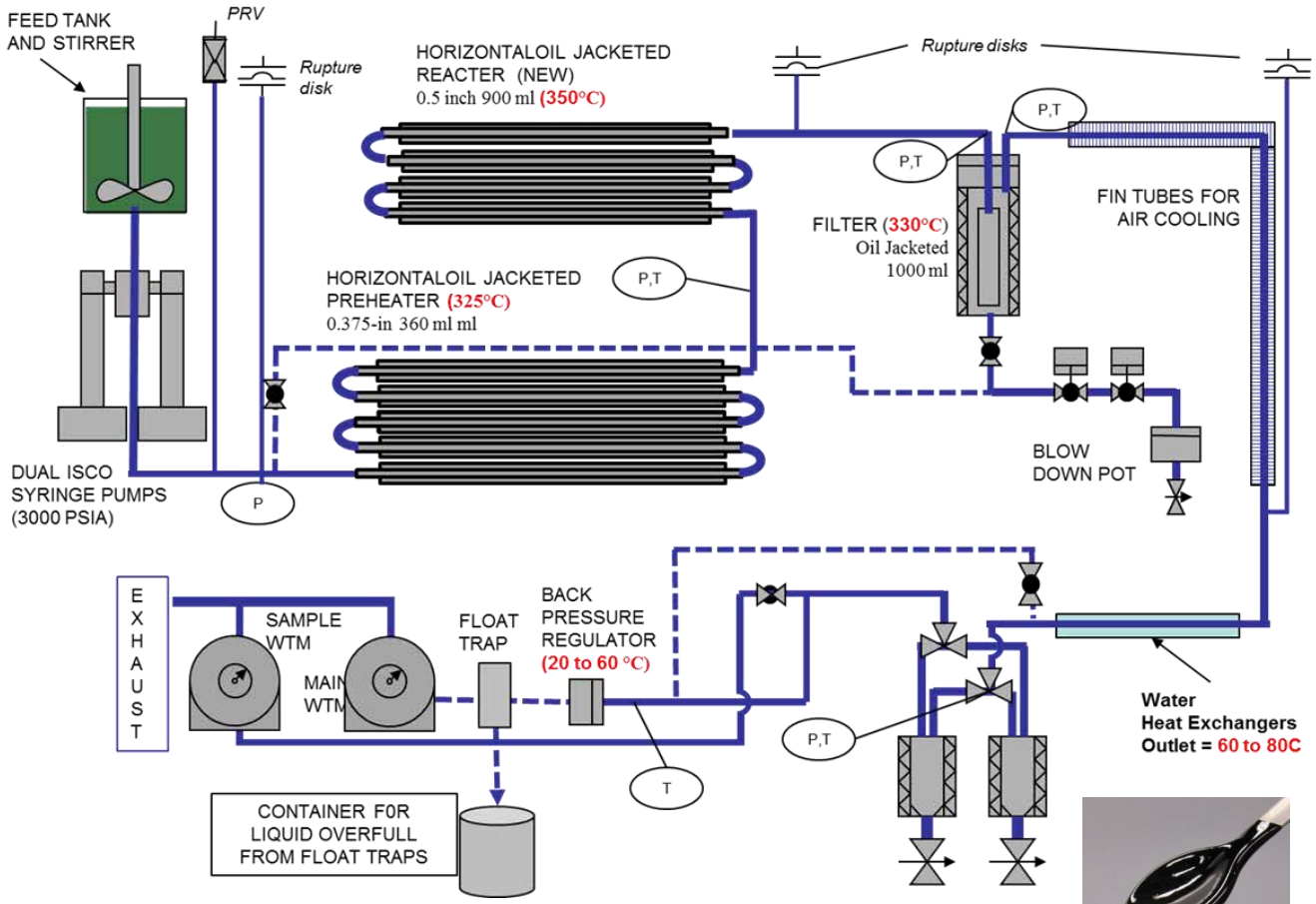
Algae Slurry (as processed)

Solids Conc. [wt%]	Ash [wt%, dry basis]	Density [g/mL]
17-26	7-28	~1.05



HTL Run Conditions

Steady state window duration: 2-3 hours
Average temperature: 330-350°C
Average pressure: 2890-2925 psig
Slurry feed rate: 1.5 L/h (LHSV=2-4 L/L/h)

Algae Biocrude (as recovered)

HTL Results from Algae Slurry

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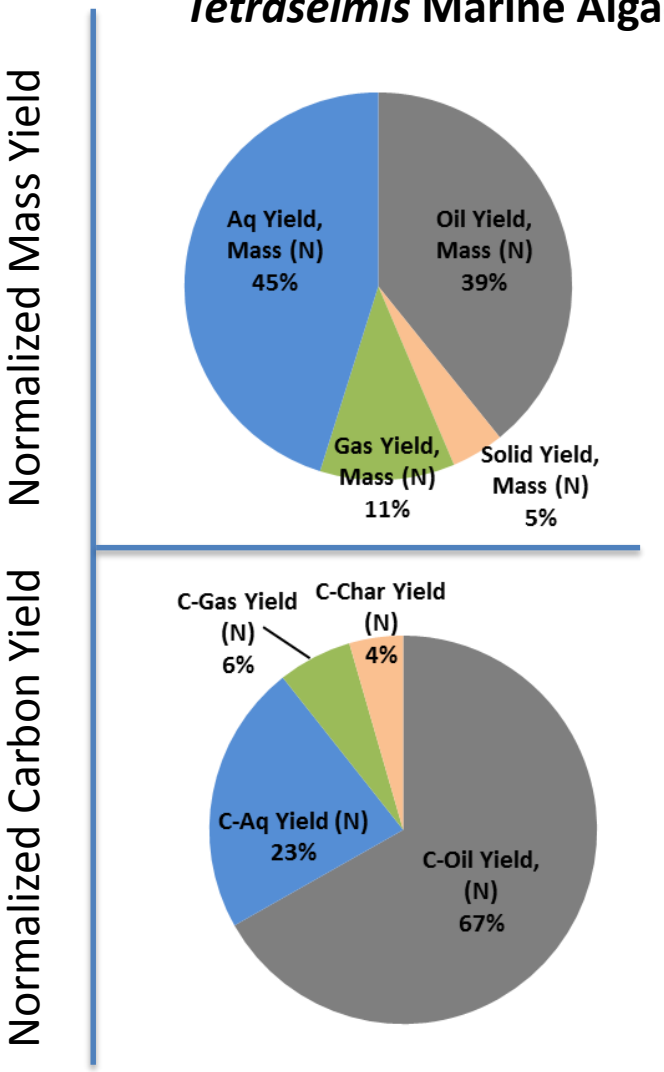
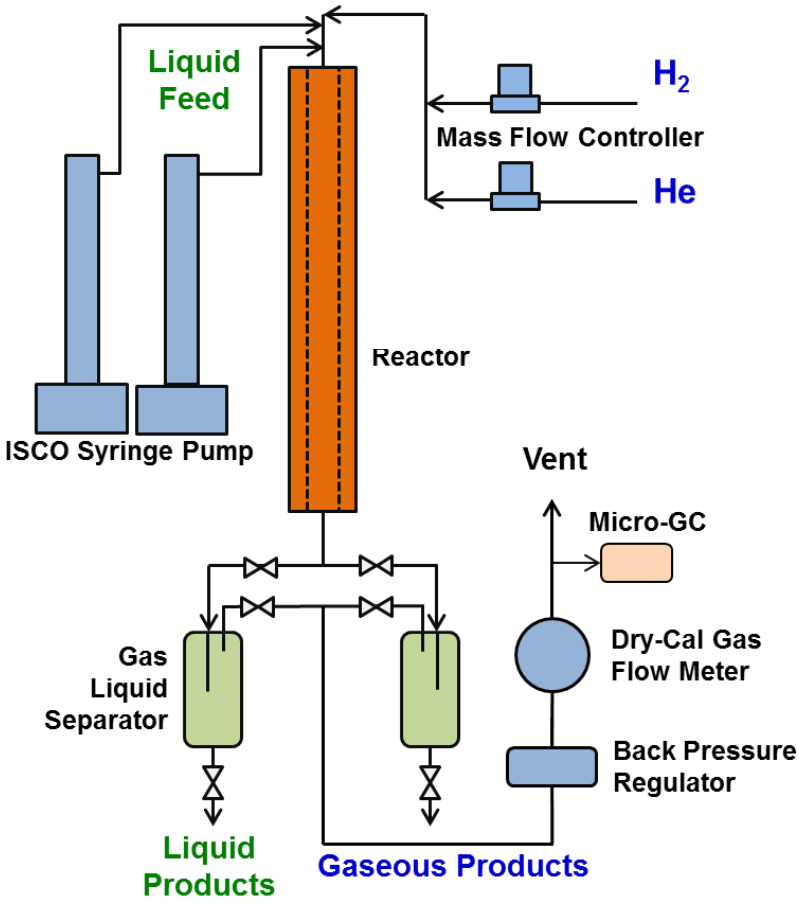
Tetraselmis Marine Algae



Biocrude Properties	
Carbon [wt% dry]	79.4
Hydrogen [wt% dry]	10.1
H:C	1.51
Oxygen [wt% dry]	3.8
Nitrogen [wt% dry]	4.8
Sulfur [wt% dry]	1.4
HHV [mJ/kg]	39.2
TAN [mg_{KOH}/g_{oil}]	54
Density [g/mL]	0.99
Viscosity [cSt, 40°C]	245
Moisture [wt%]	6.6
Ash [wt%]	0.40
Filterable Solids [wt%]	0.05

Note: The solids concentration in the Tetraselmis was 17.8 wt% DAF.

Mini-scale Fixed Bed Hydrotreater



Reactor: ½” ID, ¾” OD, 25” long, 3/16” thermal well
Heater block: aluminum sheath (3” OD, 9” length) wrapped with heating tape; insulated.

HT Product Compared to Biocrude from Algae

Analyses	*Tetraselmis*	
	Biocrude	HT (95h)
Carbon [wt%]	79.4	87.0
Hydrogen [wt%]	10.1	14.9
H:C atomic ratio	1.5	2.1
Nitrogen [wt%]	4.8	<0.05
Oxygen* [wt%]	3.8	0.9
Sulfur [ppm]	14,000	15
Moisture [wt%]	6.6	<0.5
Density [g/cm^3]	0.99‡	0.78†
Viscosity [cSt]	245‡	1.4†
TAN [mg $_{KOH}$/g]	54	<0.01

*Oxygen by difference †At 20°C ‡At 40°C

- HTL biocrude from algae can be upgraded to a hydrocarbon fuel
- Good HDN, HDO, and HDS achieved with conventional catalyst

Analytical Data for Distillate Fractions

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Sample ID#	Fraction	C	H	N	O	TAN	KF
61573-62-D1	naphtha	83.41	14.15	<0.05	0.80	<0.01	<0.5
61573-62-D2	jet	86.19	13.67	0.10	0.60	<0.01	<0.5
61573-62-D3	diesel	85.39	13.83	0.14	0.84	<0.01	<0.5

Sample ID#	Fraction	Sulfur ASTM D5453 (ppm)	Flash Point (micro-cup) °C	Cloud Pt ASTM D5773 (°C)	Pour Pt ASTM D5949 (°C)	Freezing Pt ASTM D5972 (°C)	Cetane
61573-62-D1	naphtha	18.1					
61573-62-D2	jet	12.6	49.5	-41.6	-48	-36.9	
61573-62-D3	diesel	9.4		3.2	3	4.2	58.7

Catalytic Hydrothermal Gasification

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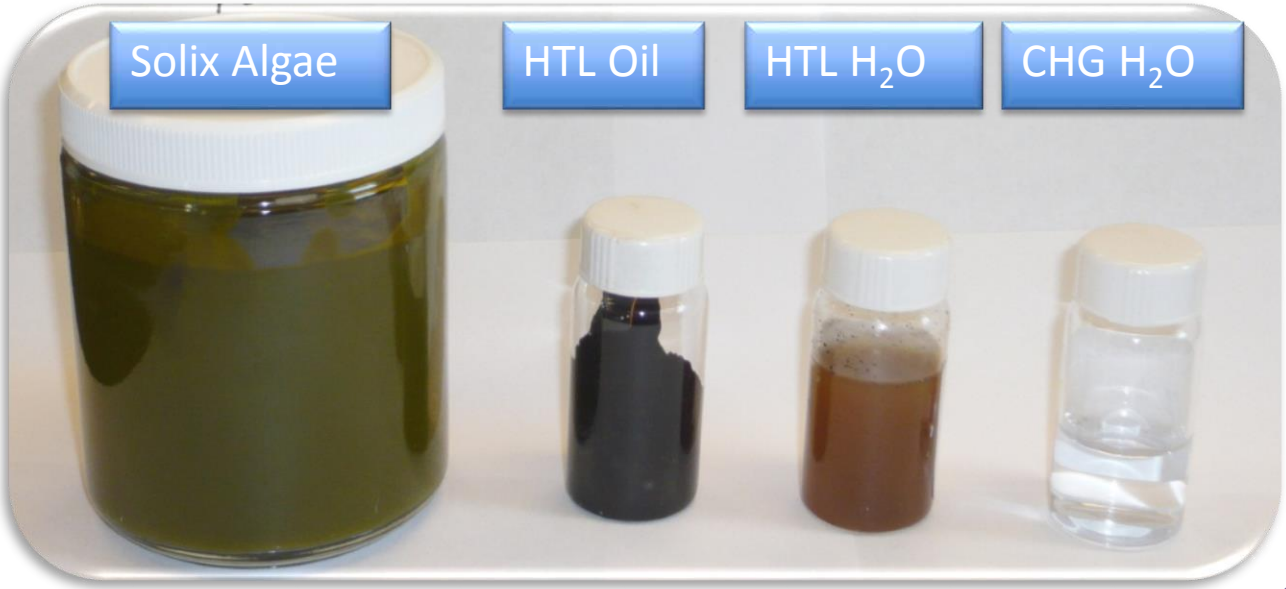
Description of CHG

- "Sister technology" to Hydrothermal Liquefaction (HTL)
- Can be used on any organic rich aqueous stream
- Produces methane gas rather than oil (catalytic action)
- Compact means to do "digestion" providing a fuel gas (CH_4/CO_2) without residual sludge
- Provides potential to recycle nutrients in biomass

Samples of Materials

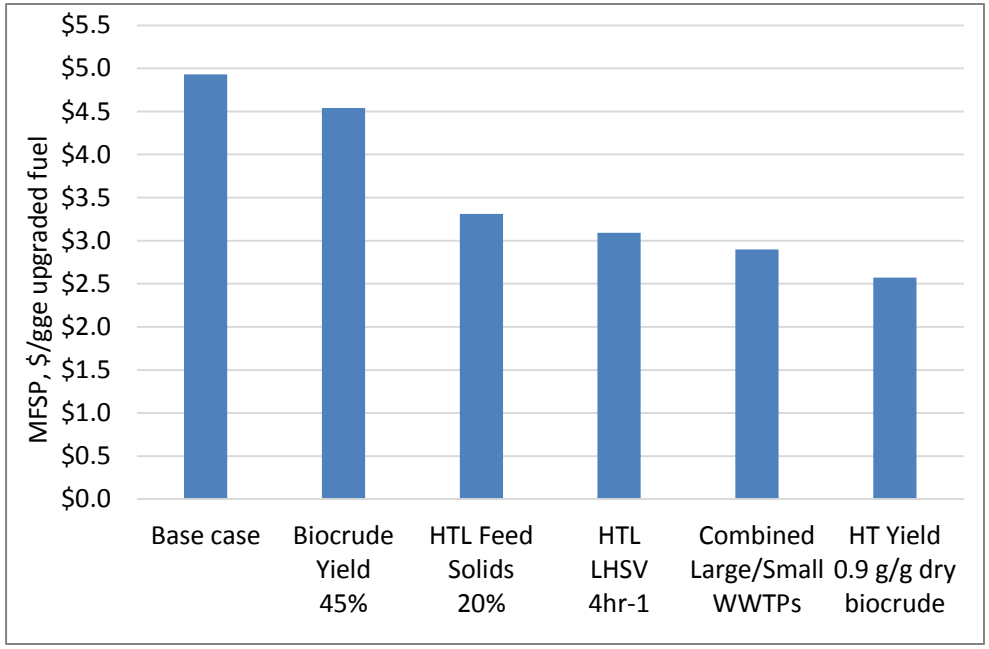
NAABB
National Alliance For Advanced Biofuels and Bio-products

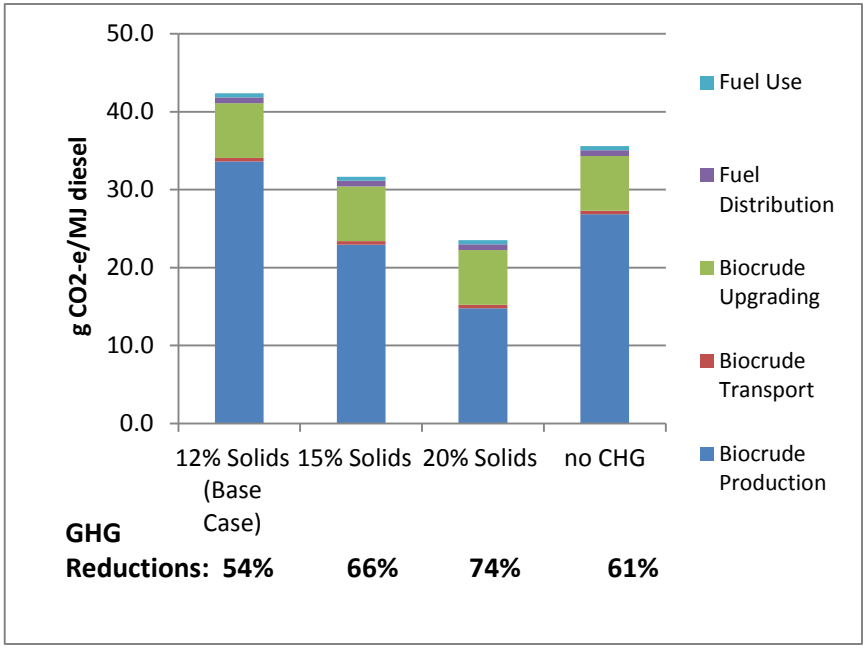


Partner

Genifuel

Preliminary Algae TEA – Potential Improvements & Preliminary LCA





- Increased yields, solids loading, and reactor space velocity are possible with further testing.
- Combined improvements could reduce fuel MFSP by about half.
- Solids loading impacts GHGs (and $).
- Reduction from petroleum fuel is >50% for all cases.

TEA Cost Variability

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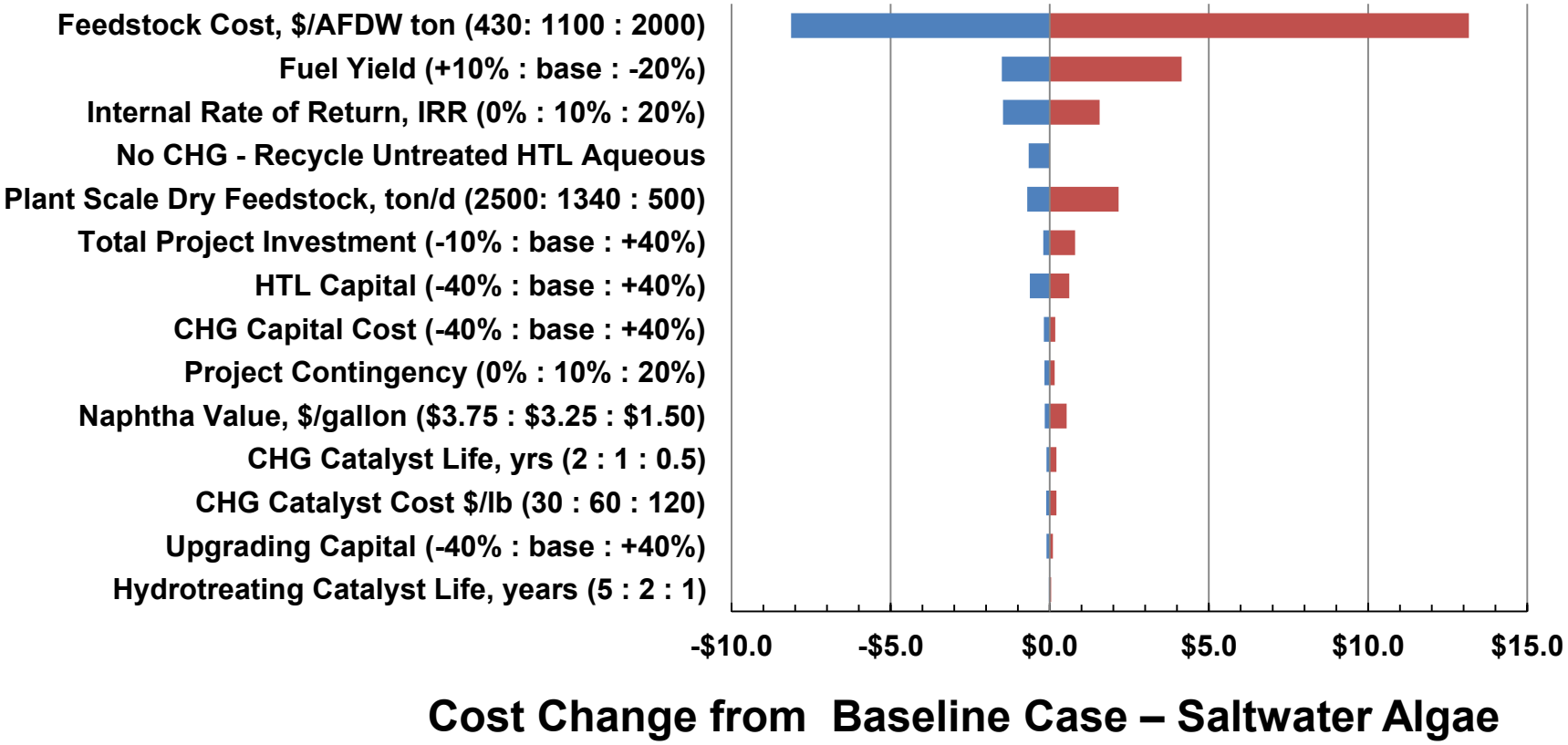

Cost Change from Baseline Case – Saltwater Algae

Techno-Economic Analysis of Whole Algae Hydrothermal Liquefaction (HTL) and Upgrading System: Freshwater versus Saltwater Algae
Y Zhu, S B Jones, D B Anderson, R T Hallen, A J Schmidt, K O Albrecht, D C Elliott
2015 Algae Biomass Summit, September 29 - October 2, 2015 Washington, DC

Scale-Up and Technology Transfer

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- Genifuel is the PNNL licensee.
- Federal Laboratory Consortium Award for Excellence in Technology Transfer
- R&D100 Award
- Engineering challenges remaining include;
  - slurry pumping,
  - efficient separations,
  - heat integration

Jim Oyler with the 1000 L/day (of 20 wt% BDAF) Hydrothermal Processing Pilot System

continuous HTL/CHG system for algal feedstock

NAABB-Reliance-PNNL-Genifuel

Scale-Up and Technology Transfer

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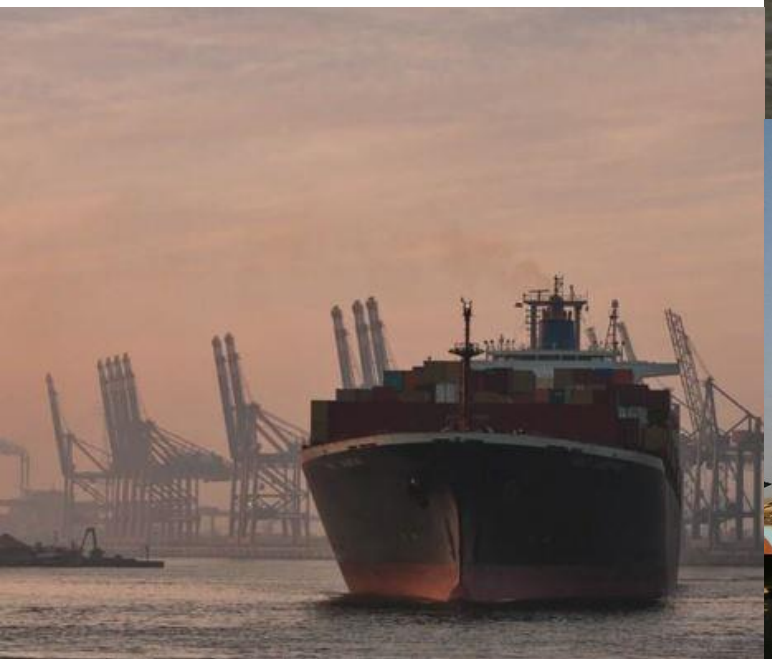
- **HPPS -- Made in America**
  - Technology developed at PNNL
  - System design by Genifuel
  - Assembled in Colorado
  - Shipped to India
  - On-site at RIL.



Scale-Up and Technology Transfer

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- Being installed at the RIL algae processing site in Gagva, India
  - Expected start-up Q3 2016
- Near Jamnagar
  - Largest petroleum refinery complex in the world