Pacific Northwest
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Challenges and Opportunities for Hydrothermal Liquefaction of Macroalgae

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What is HTL and why do we care?

Hydrothermal liquefaction (HTL) is…

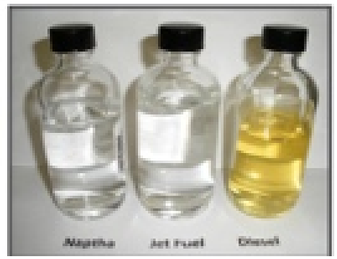
the thermochemical conversion of biomass in a hot, pressurized water environment to break down solid biopolymer structures to predominantly liquid components

It stands out among thermal conversion processes because…

- HTL is a conceptually simple (i.e., heated pipe), scalable, and robust continuous process that can accept a diverse range of wet feedstocks (no drying!)
- HTL results in high carbon yields to liquid hydrocarbons (up to 60%)
- HTL produces a gravity-separable biocrude with low oxygen content (5–15 %) that can be upgraded in a single stage hydrotreater

HTL Conditions
Temp: 330-350°C
Pressure: 2900 psig
t_{res}: 10-30 min

Hydrotreating Conditions
Temp: 400°C
Pressure: 1500 psig H_2
Sulfided Catalyst



Wet biomass material (algae, sludge, manure) → Stable biocrude oil (up to 60% C-yield) → Fuel Blendstocks (95%+ C-yield)

HTL Process Development Timeline Spans Decades and Includes Wood, Algae, and Wet Waste

1970s Process Development

- Batch and Model Compounds

1980s Pilot Demonstrations for Woody Feedstocks

- Albany
- Shell HTU
- PERC, LBL

2008-2010 Renewed Process Development

- Continuous-Flow Process
- No Reducing Agent
- Agricultural Residues

US DOE Consortia

- **2011-2014** NABC for wood
- **2010-2013** NAABB for microalgae

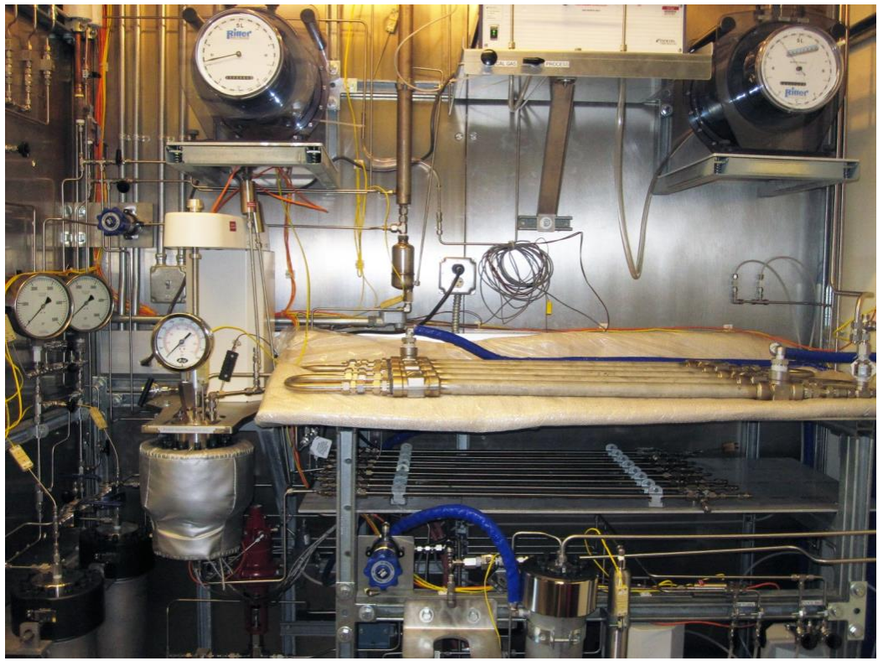
2014-Present Process Scale-up

- Genifuel
- PNNL
- bio2oil
- Steeper
- Licella

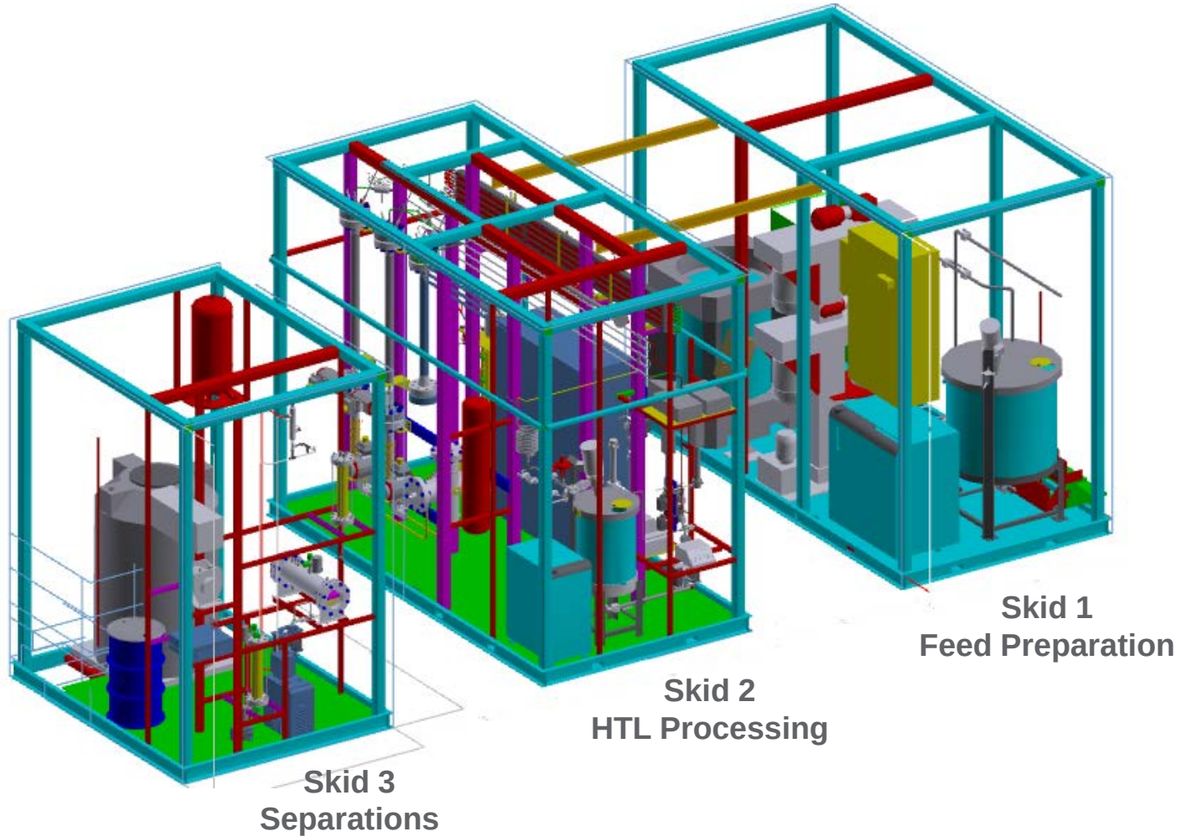
2015-Present Expanded Range of Feedstocks

Wet wastes such as sludge, manure, food waste

We have successfully scaled the process from bench to engineering scale (~5x)



Bench-scale continuous HTL reactor system, slurry flow 2 to 6 L/h



Modular HTL system, slurry flow 12 to 16 L/h
Integrated cross-flow heat exchange
Continuous pressure letdown and separations

HTL of kelp led to lower biocrude yields but showed promise for nutrient recovery (N,P,K)

- Continuous HTL tests of 6 samples of Saccharina spp. collected by PNNL dive team
- Low starting solids concentration (5-10%) and high ash content (20-40%) led to low biocrude mass yields (<20%, daf)
- Thermal pretreatment at 175 °C allowed dewatering to 22% solids with a resulting biocrude mass yield of 27% (daf)
- Aqueous phase was treated with CHG
- Phosphorus precipitated in reactor solids and presumed to be recoverable (bio-available)
- Nitrogen split between products, but recoverable as ammonia from aqueous fractions; potassium remained in solution

Saccharina japonica on ropes in northwest China (photograph © Dr D.L. Duan Delian; courtesy Zi-Min Hu)

Reference: Elliott et al., ACS Sustainable Chem. Eng. 2014, 2, 207-215.

Catalytic hydrothermal gasification (CHG) can treat the aqueous phase and recover energy and nutrients

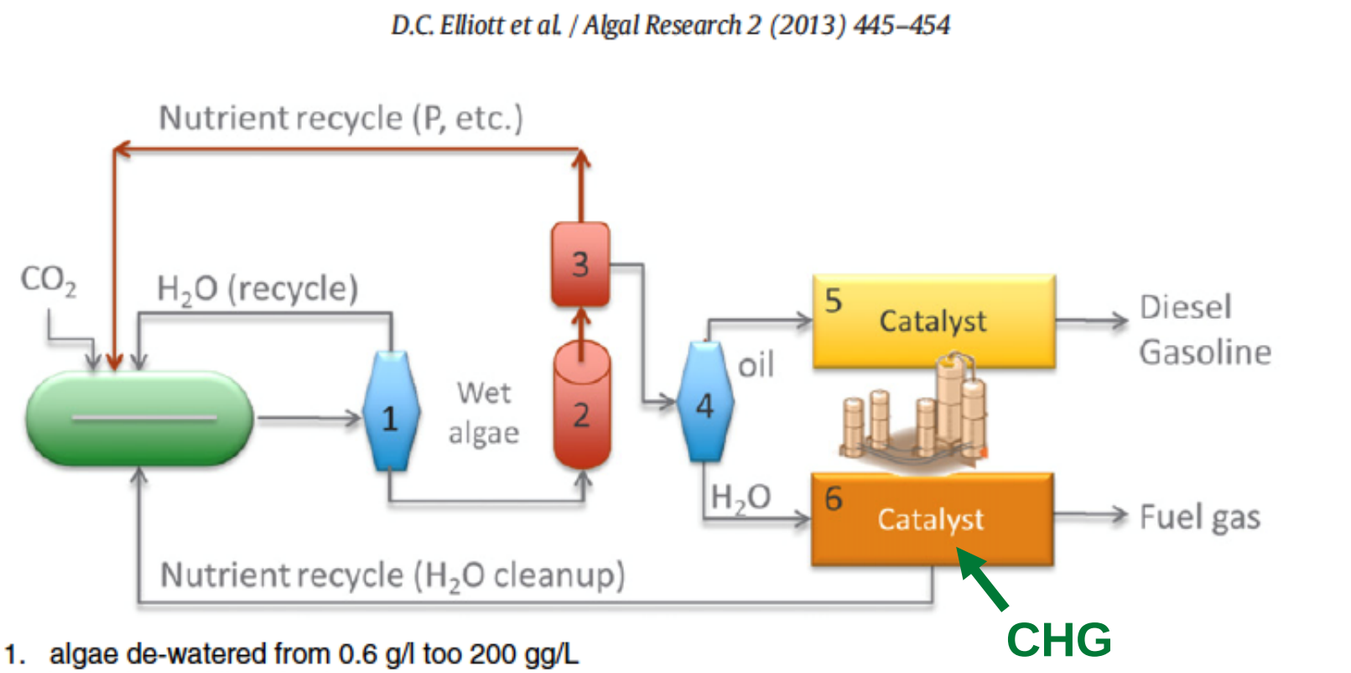


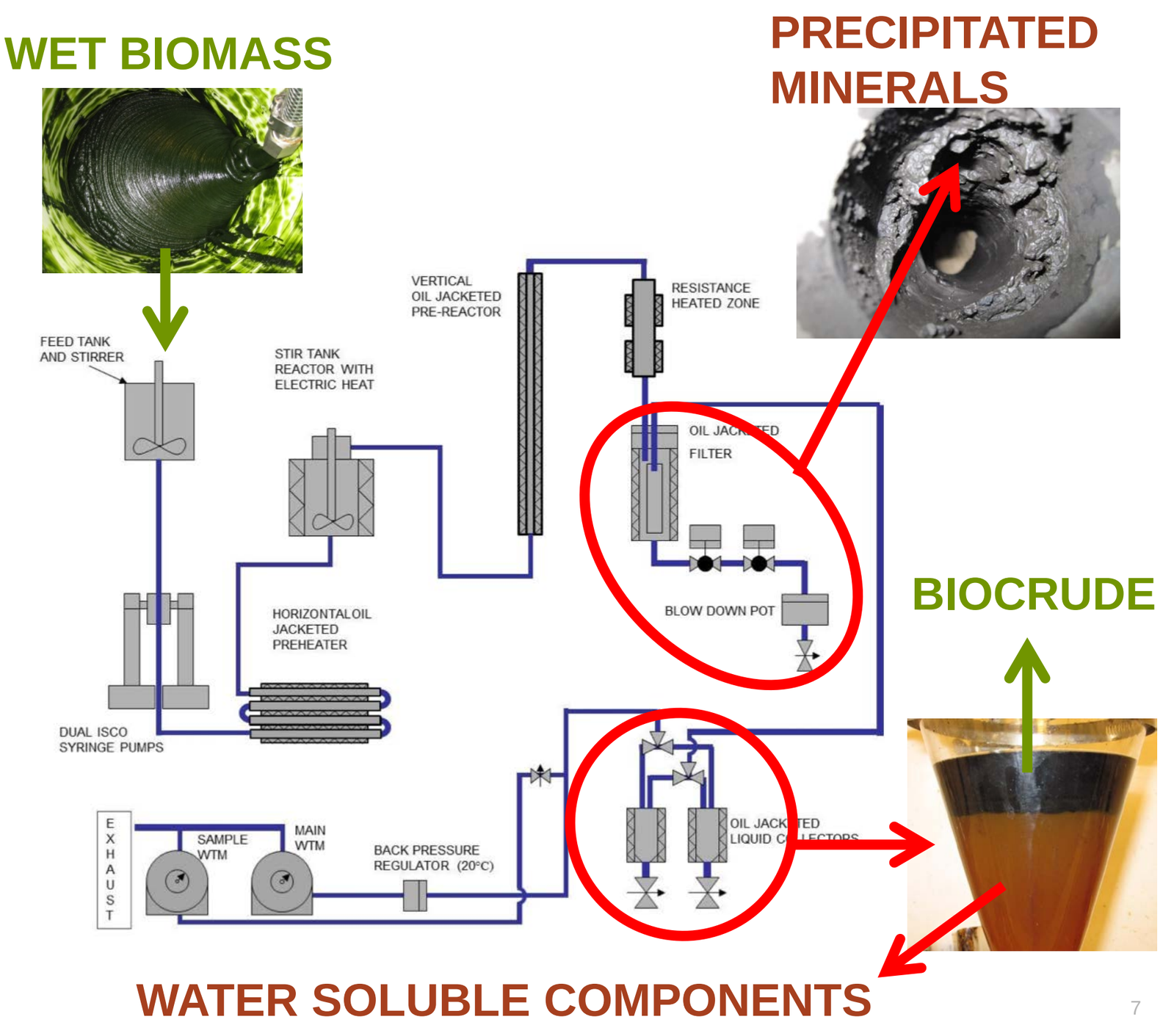
Fig. 9. Process scheme utilizing algae growth and hydrothermal processing for fuels.

- Original integrated process included CHG for the HTL aqueous phase to recover fuel gas (CH_4/CO_2) and ammonia
- CHG was determined to be cost-prohibitive for microalgae due to sulfur poisoning of the catalyst
  - *f* Sulfur-tolerant CHG catalysts are under development
  - *f* High Nitrogen?

Nutrient Recovery from Hydrothermal Processing

- **Nitrogen** primarily reduced to ammonium and partitions to the aqueous waste
- **Phosphorus** and **iron** precipitate into the solid phase waste fraction

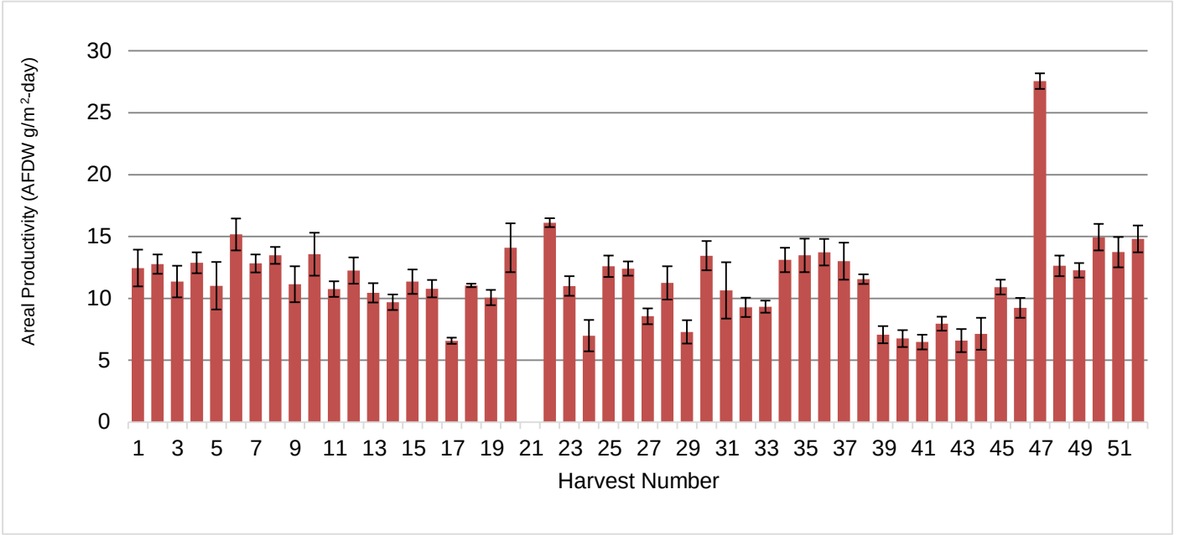
Edmundson et al.
Algal Research 26 (2017) 415–421



Results of Water and Nutrient Recycle Testing

- All **Nitrogen, Phosphorus, and Iron** can be replaced with nutrients derived from the by-products of HTL processing
- **DIRECT** recycle of HTL aqueous phase for **N** eliminates need for treatment of HTL aqueous phase (and thus, CHG)
- Over 350 days of continuous cultivation water recycle for chlorella sorokiniana
- Additional algal strains have been screened for tolerance to direct recycle of HTL derived nutrients

Complete Media Recycle Using HTL Derived Nutrients



Initial Strain Screening Using HTL Derived Nutrients

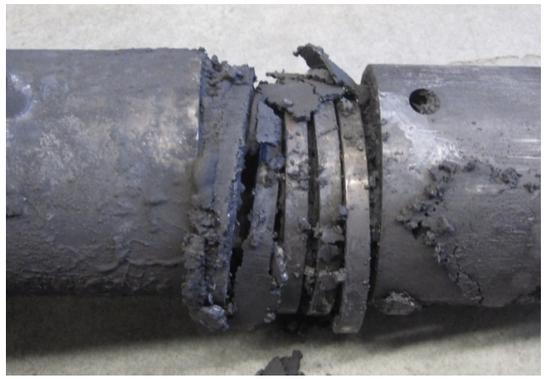
Strain (Genus species)	Relative HTL Tolerance
Chlorella sorokiniana DOE1412.HTL	113.0
Nannochloropsis oceanica CCAP849/10	108.5
Tetraselmis sp. (LANL isolate)	87.0
Stichococcus minor CCMP819	41.6
Chlorella vulgaris LRB-AZ1201	27.2
Nannochloris sp. NREL-38	20.7
Acutodesmus obliquus UTEX393	17.4
Choelastrella sp. DOE0202	14.9
Scenedesmus sp. NREL-46B	3.5
Monoraphidium minutum 26-AM	3.4
Tisochrysis lutea CCMP1324	2.4

But won’t it corrode the reactor?

Materials of construction evaluation with ORNL

- In-situ: reactor parts, rings, coupons for hundreds of hours
- Ex-situ: coupons and U-bend pieces (stress) in liquid and vapor space
- Findings: little corrosion for 304L, 316L, and 321 stainless steels, no evidence of Cl- stress corrosion cracking

Rings of 304L, 310, 316L and 321 stainless steels and alloy 825



Rings installed in HTL CSTR Reactor

Glass system with reflux used for 50 and 75° & : Coupons located in immersed aqueous and in vapor phase

Ex-Situ

Coupons & U-bend

316-L U-bends on preheater removed from service