Pacific Northwest
NATIONAL LABORATORY

Challenges and Opportunities for Hydrothermal Liquefaction of Macroalgae

Dan Anderson, Justin Billing, Andy Schmidt
Scott Edmundson, Yunhua Zhu

Energy & Environment Directorate
Richland, WA

ARPA-E Workshop, November 18, 2020
PNNL-SA-158056

U.S. DEPARTMENT OF ENERGY BATTELLE

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

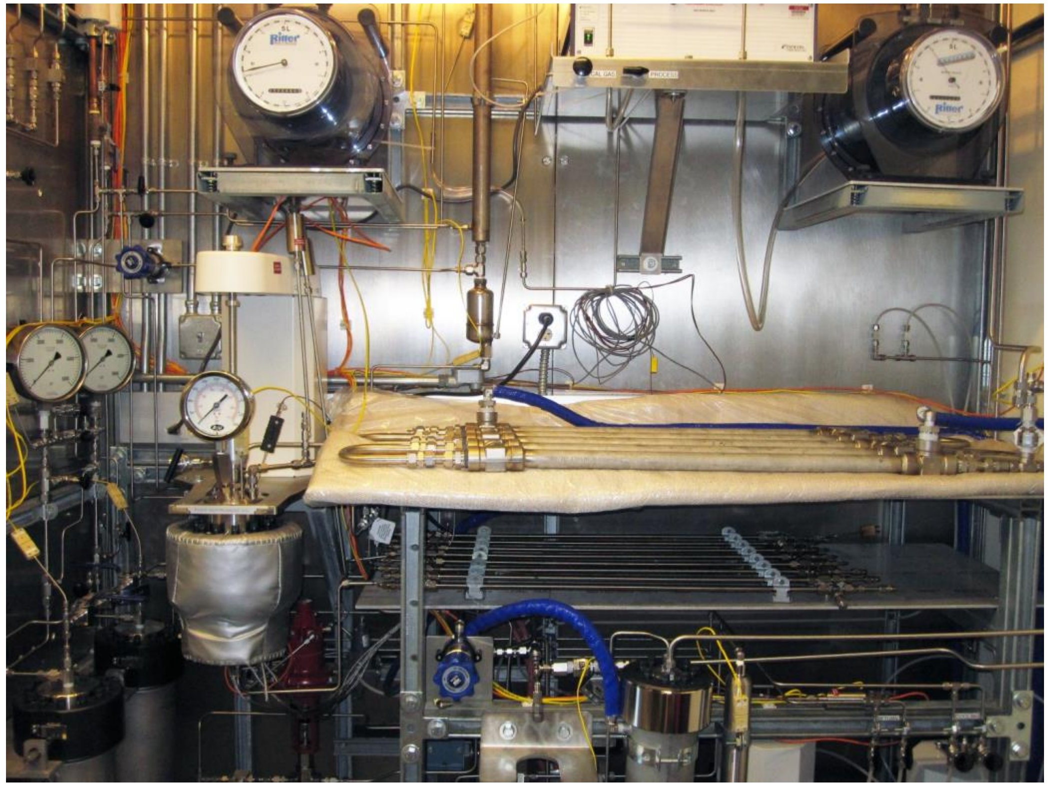
2014-Present Process Scale-up

- Genifuel
- PNNL
- bio2oil
- Steeper
- Licella

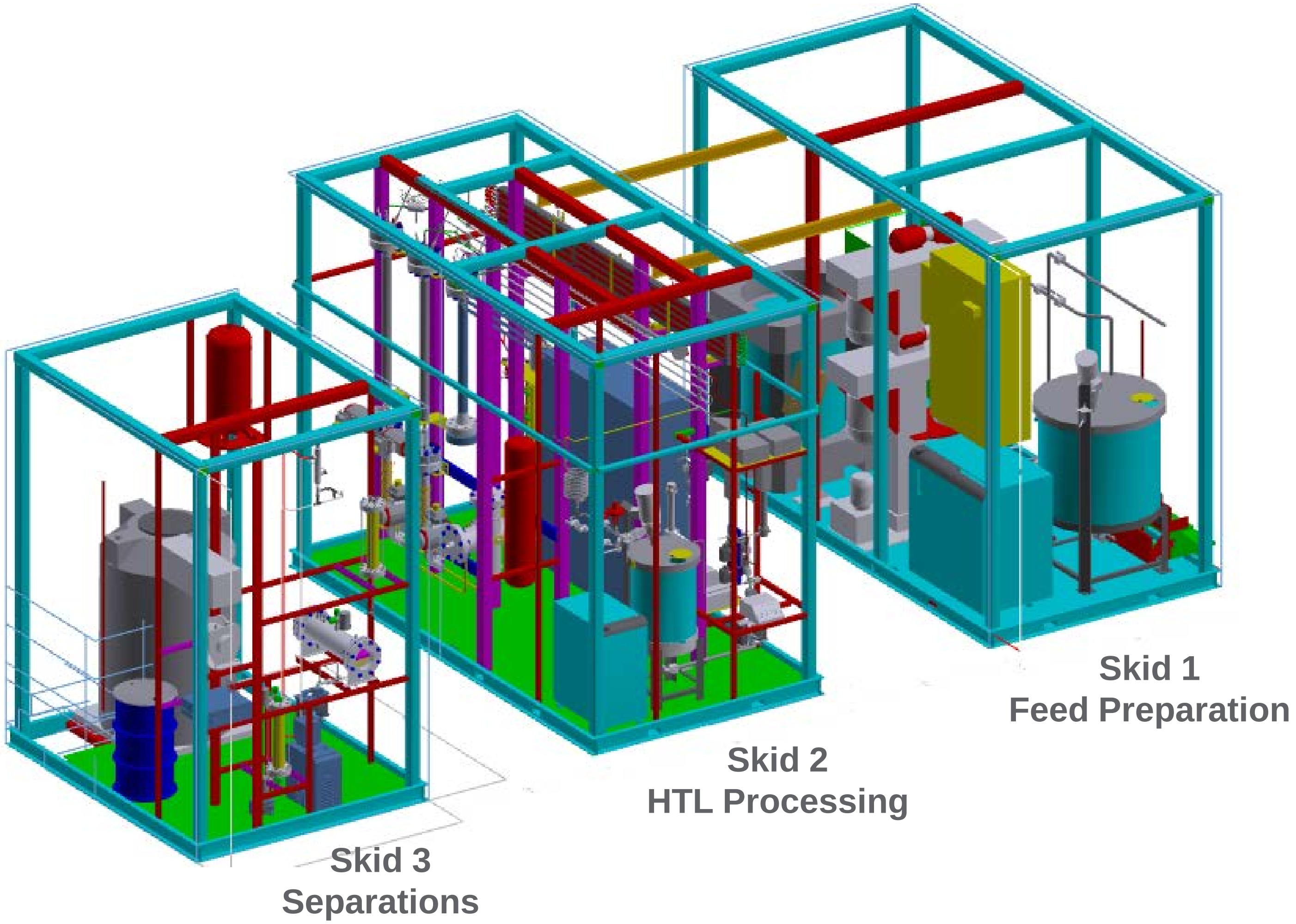
2015-Present Expanded Range of Feedstocks

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

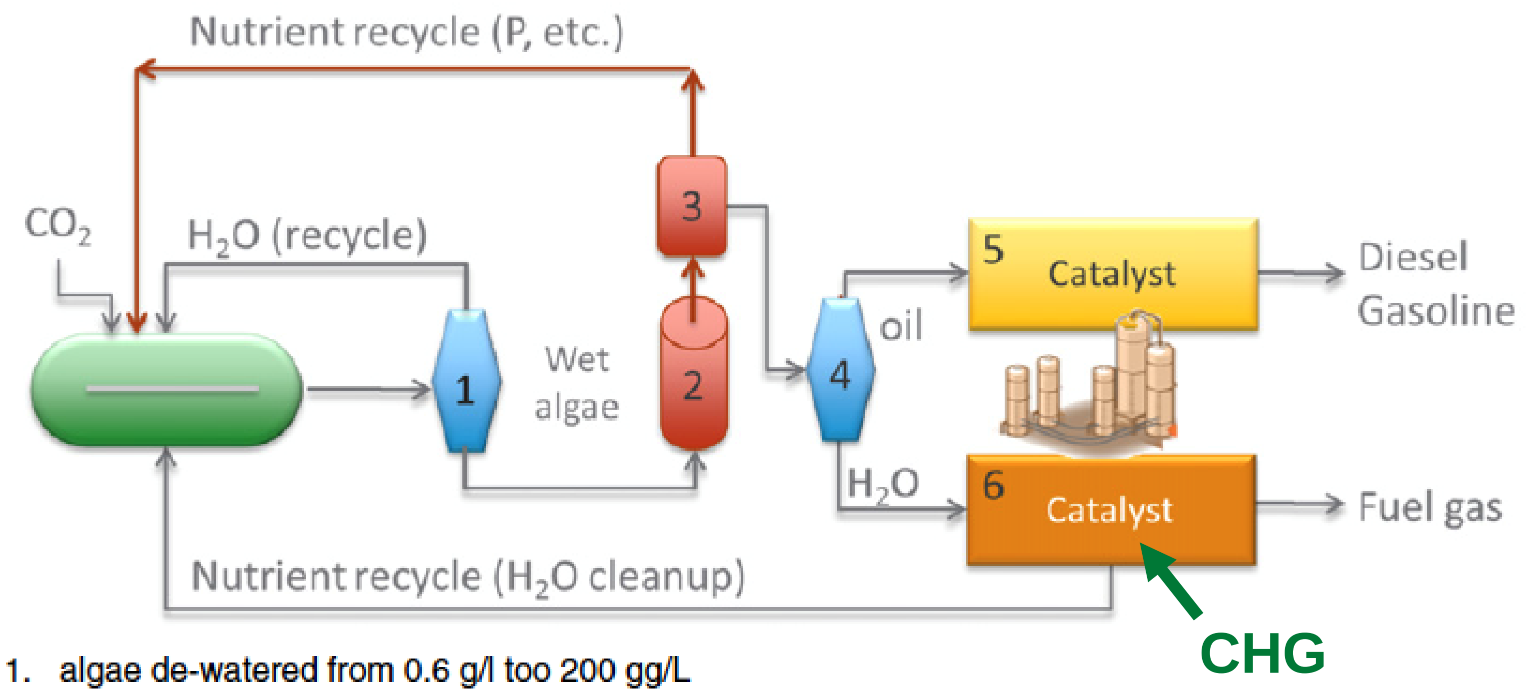
Saccharina japonica on ropes in northwest China (photograph © Dr D.L. Duan Delian; courtesy Zi-Min Hu)

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

Pacific Northwest
NATIONAL LABORATORY

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

D.C. Elliott et al. / Algal Research 2 (2013) 445–454



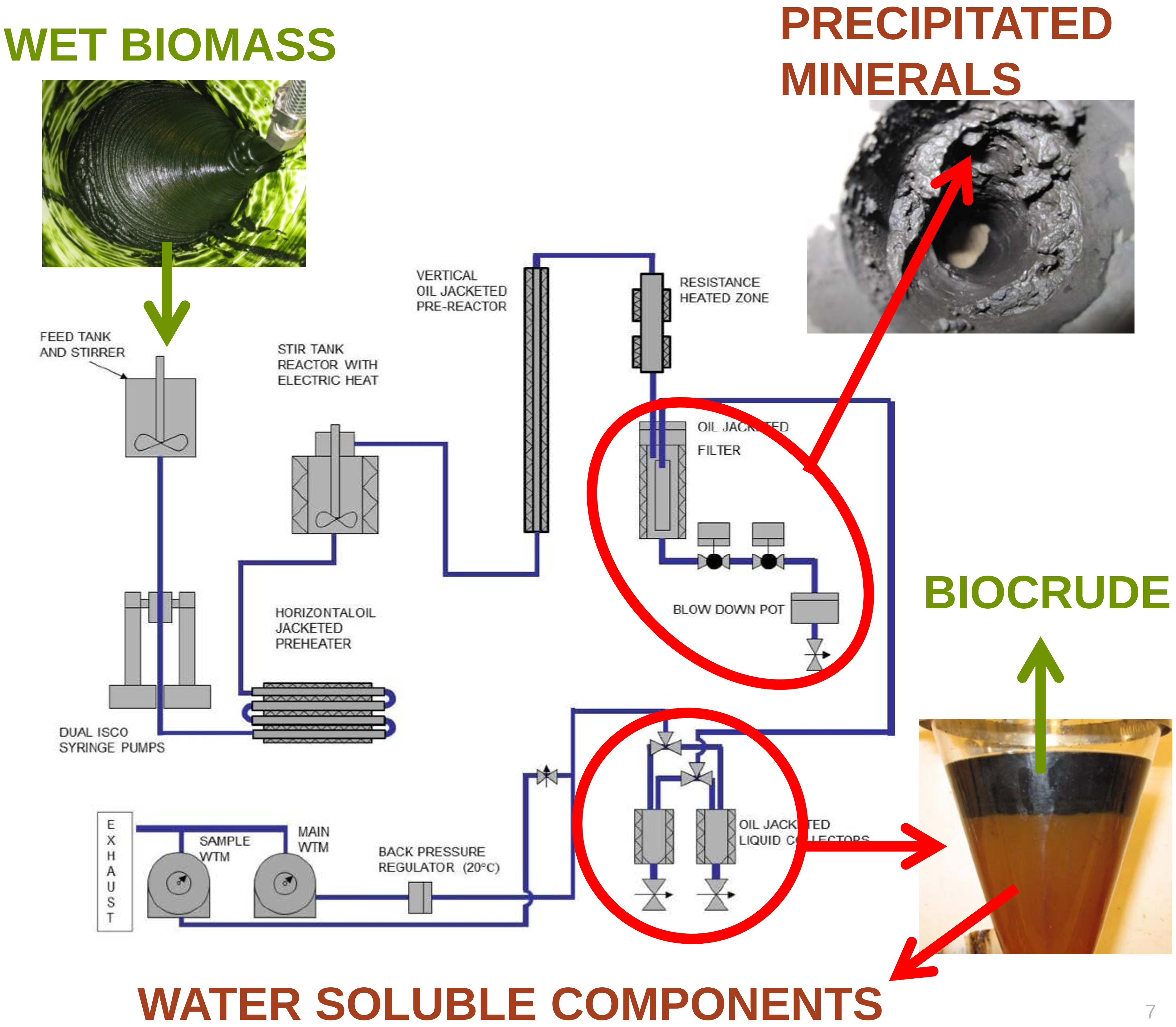
1. algae de-watered from 0.6 g/l too 200 gg/L
2. hydrothermal liquefaction
3. solid precipitate separation for clean bio-oil production and phosphate cappturre
4. oil/water phase separate
5. oil hydrotreater to produce hydrocarbons—diesel/gasoline)
6. aqueous phase carbon is catalytically converted to fuel gas and nutrients recycled (N, K, some CO_2, etc)

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
  - Sulfur-tolerant CHG catalysts are under development
  - 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

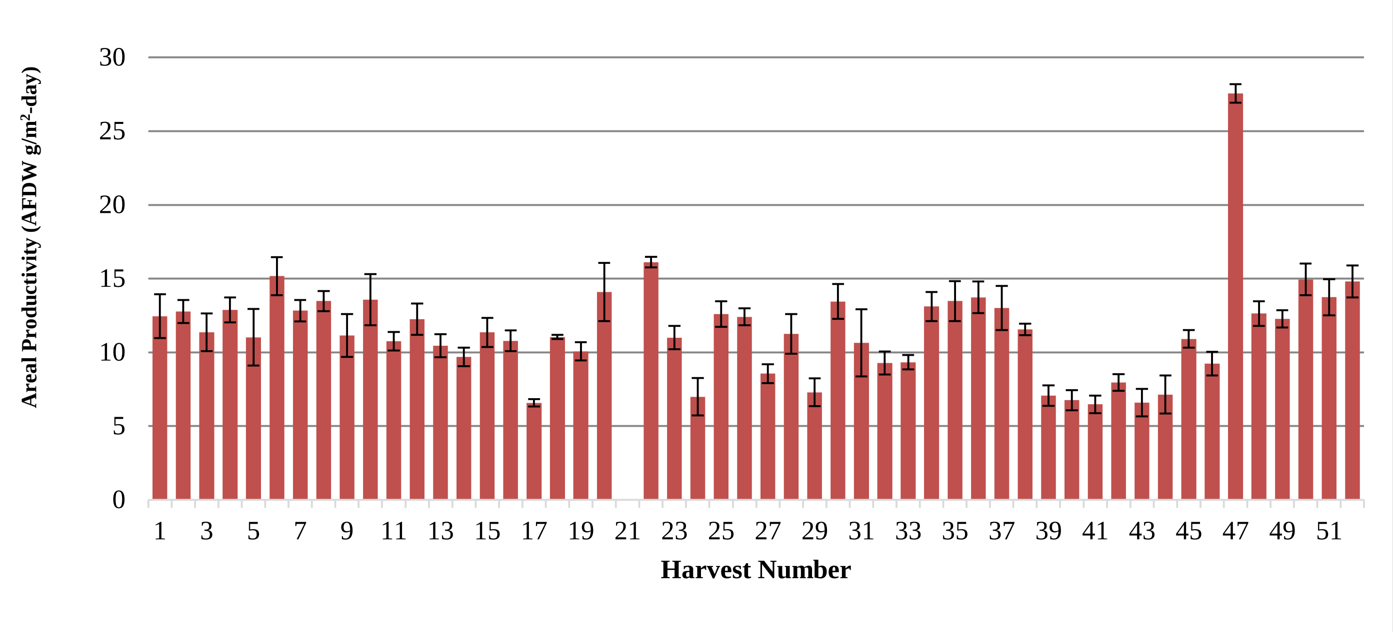


Edmundson et al.
Algal Research 26 (2017) 415–421

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. NREL39-A8	20.7
Acutodesmus obliquus UTEX393	17.4
Choelastrella sp. DOE0202	14.9
Scenedesmus sp. NREL46B-D3	3.5
Monoraphidium minutum 26B-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

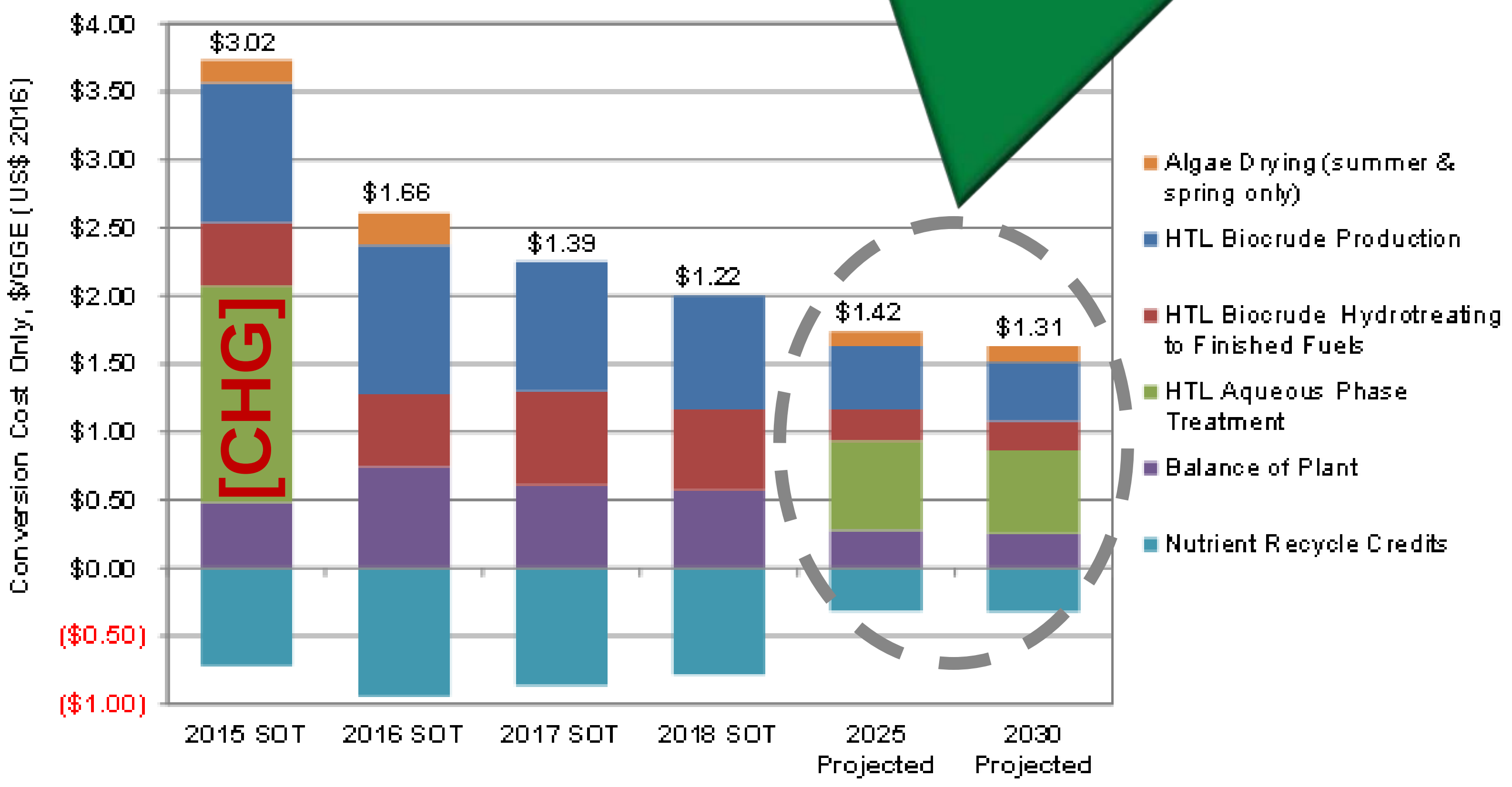
Glass system with reflux used for 50 and 75°C → Coupons located in immersed aqueous and in vapor phase

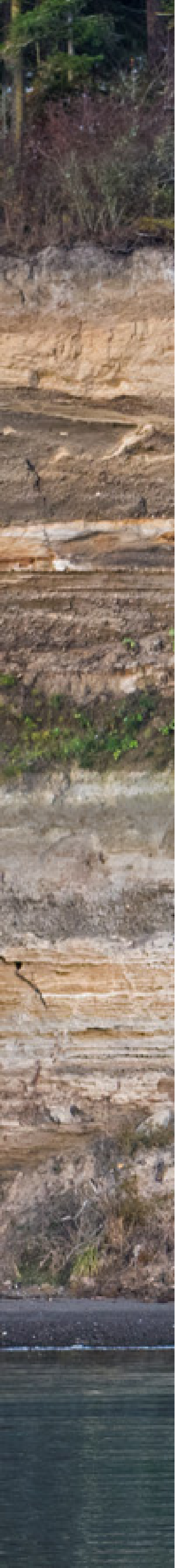
316-L U-bends on preheater removed from service

Technoeconomic analysis shows that 2025 and 2030 projected HTL conversion cost targets have already been met

- Biomass conversion costs are based on PNNL research into HTL conversion, biocrude upgrading, and HTL aqueous testing
- Demonstrating full nutrient recycling and avoiding water treatment by CHG (2016) led to deep net cost reductions
- **Where to go next?**

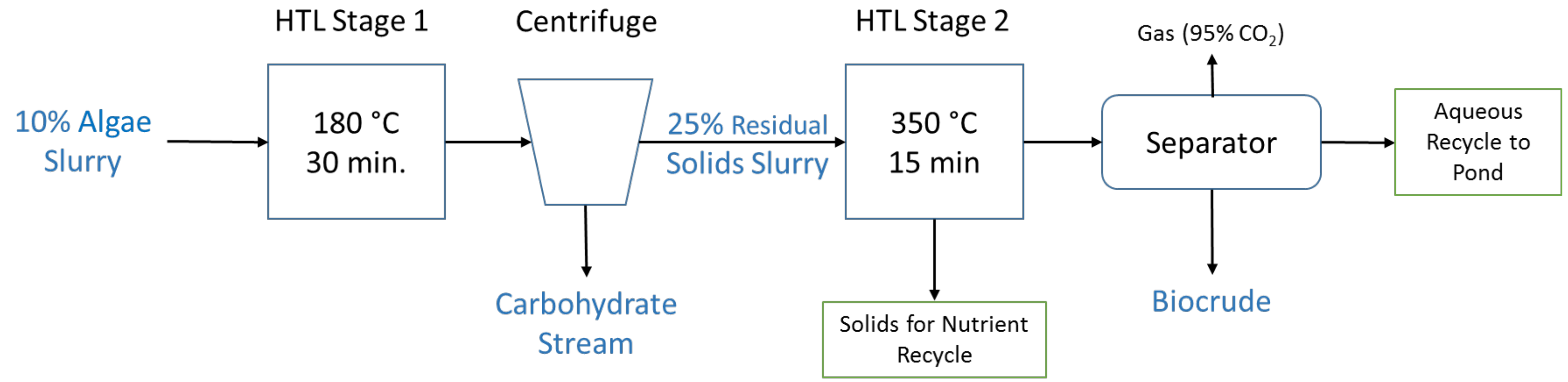
- Out-year cost targets from the HTL Design Case published in 2014 **have already been met**
- A new design case outlining strategies for additional cost reductions slated for FY20 publication



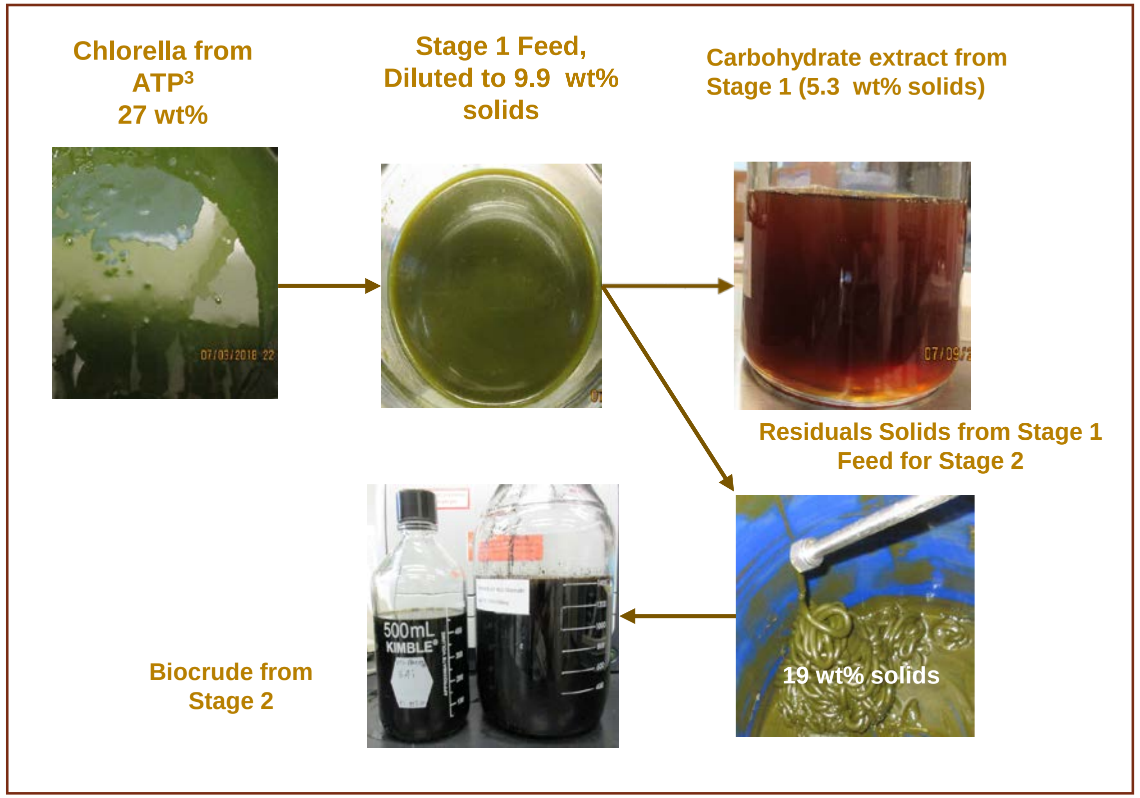


Sequential HTL enhances biocrude yield from algae residuals and produces carbohydrate stream

General Process Flow Diagram

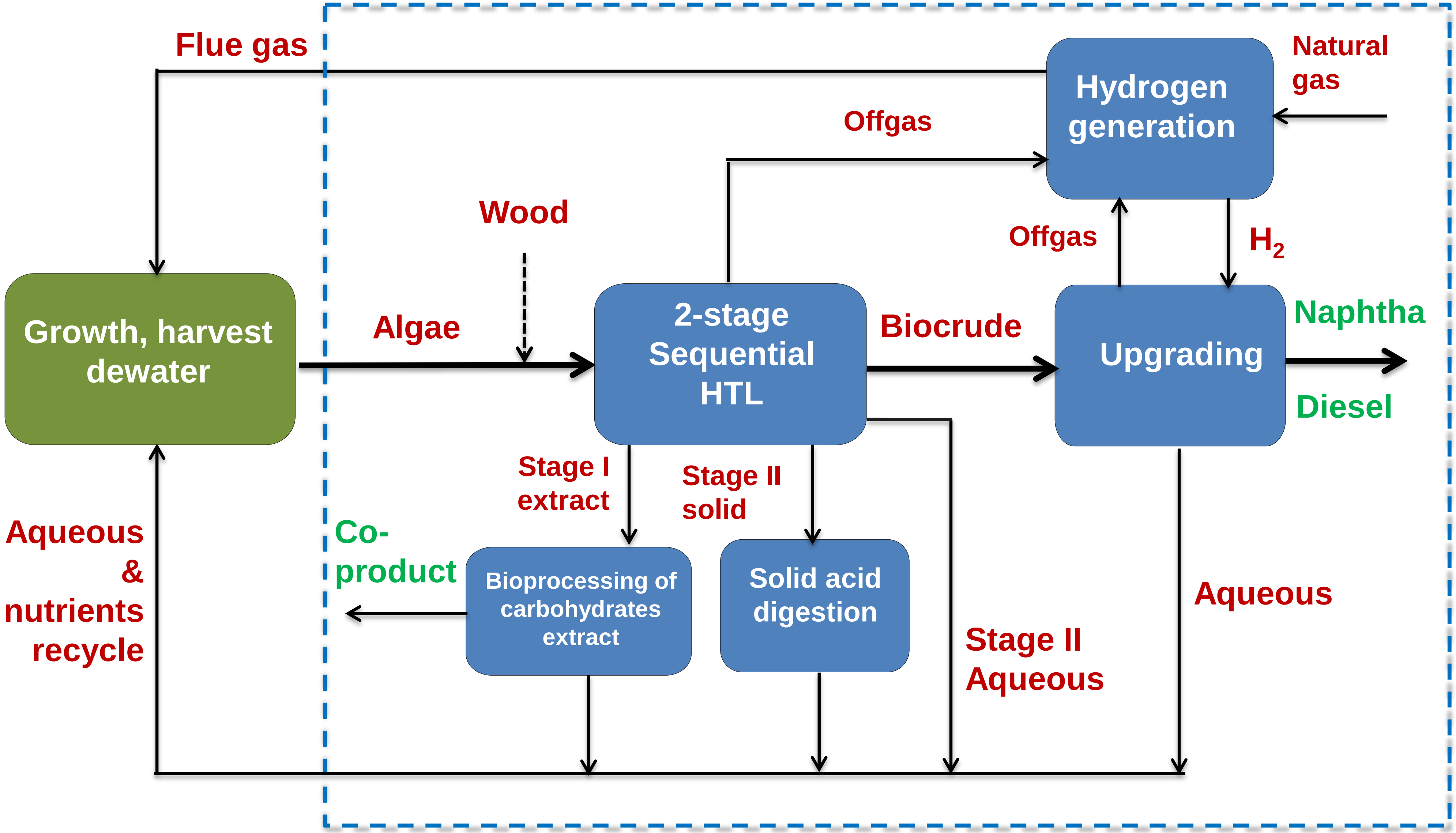


- Stage 1 Extraction
  - Yields usable sugars for co-product production
  - Provides improved residual biomass for fuel conversion
- Stage 2 Conversion
  - Results in higher biocrude yields and quality from higher solids feed, lower ash and carbohydrates
- Sequential HTL Processing Progress
  - Technical feasibility proven
  - Update of the algae HTL design case (2020) is based on sequential HTL



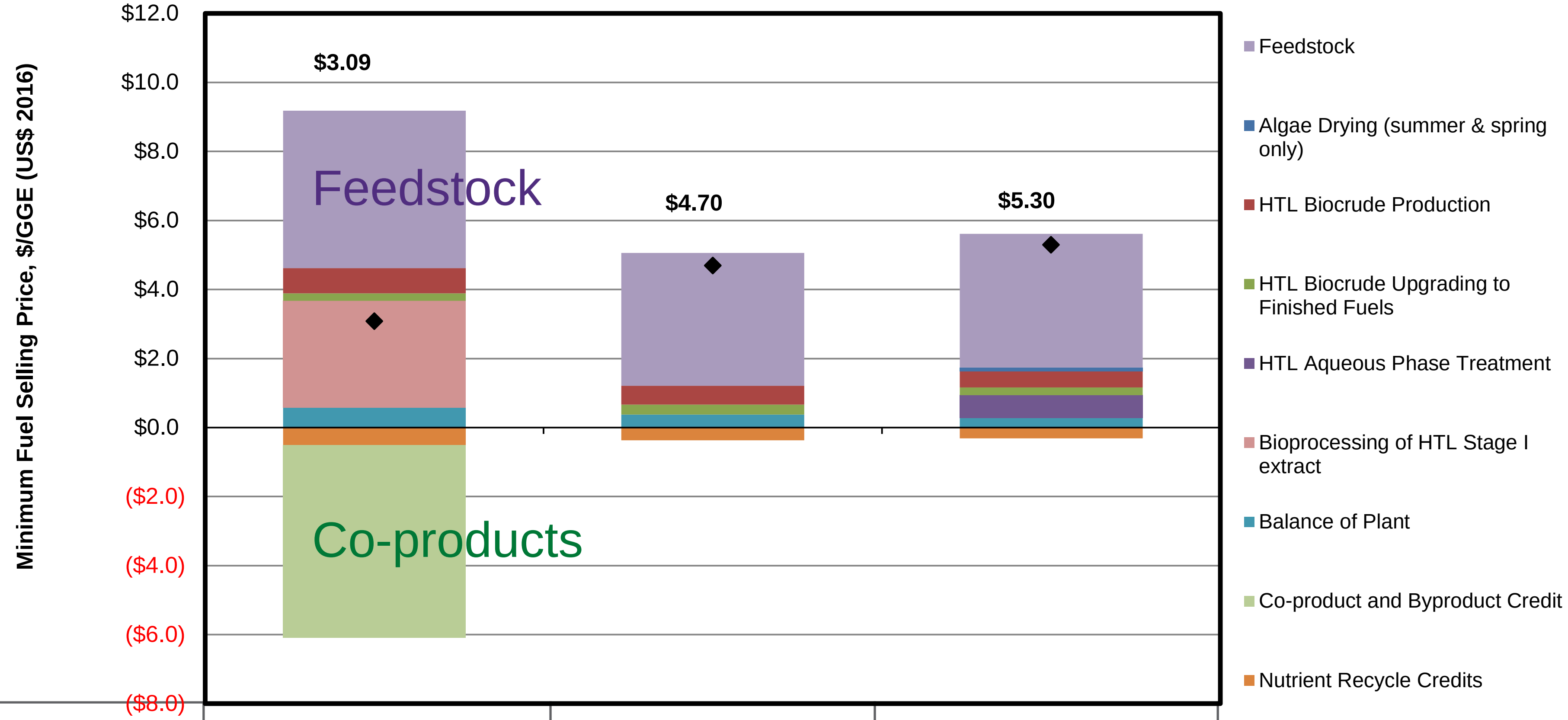
Material Flow in Sequential HTL

Algae HTL 2020 design case features sequential HTL to meet programmatic cost targets



- Initial algae HTL based on single-stage high-temperature conversion.
- Further cost improvements for the single-stage HTL system are limited
- PNNL proposed and tested two-stage sequential HTL to meet future cost targets

Sequential HTL co-products help offset feedstock costs



Processing Area Cost Contributions	2020 design case (SEQHTL-2025 projection)	Single-stage HTL (blended feed, 2025 projection)	2014 design case (algae only, single-stage HTL, 2025 projection)
Feedstock	→ $4.57	$3.85	$3.87
Algae Drying (summer & spring only)	$0.00	$0.00	$0.11
HTL Biocrude Production	$0.73	$0.55	$0.47
HTL Biocrude Upgrading to Finished Fuels	$0.21	$0.28	$0.23
HTL Aqueous Phase Treatment	$0.00	$0.00	$0.66
Bioprocessing of HTL Stage I extract	$3.10	$0.00	$0.00
Balance of Plant	$0.58	$0.38	$0.28
Co-product and Byproduct Credit	→ ($5.58)	$0.00	$0.00
Nutrient Recycle Credits	($0.52)	($0.37)	($0.32)
Minimum Fuel Selling Price, $/GGE	**$3.09**	**$4.70**	**$5.30**

Sequential HTL can be applied to macroalgae feedstocks

Sequential HTL

Stage 1
<200 °C

- Polysaccharides for fermentation
- Solid residual to Stage 2

Stage 2
350 °C

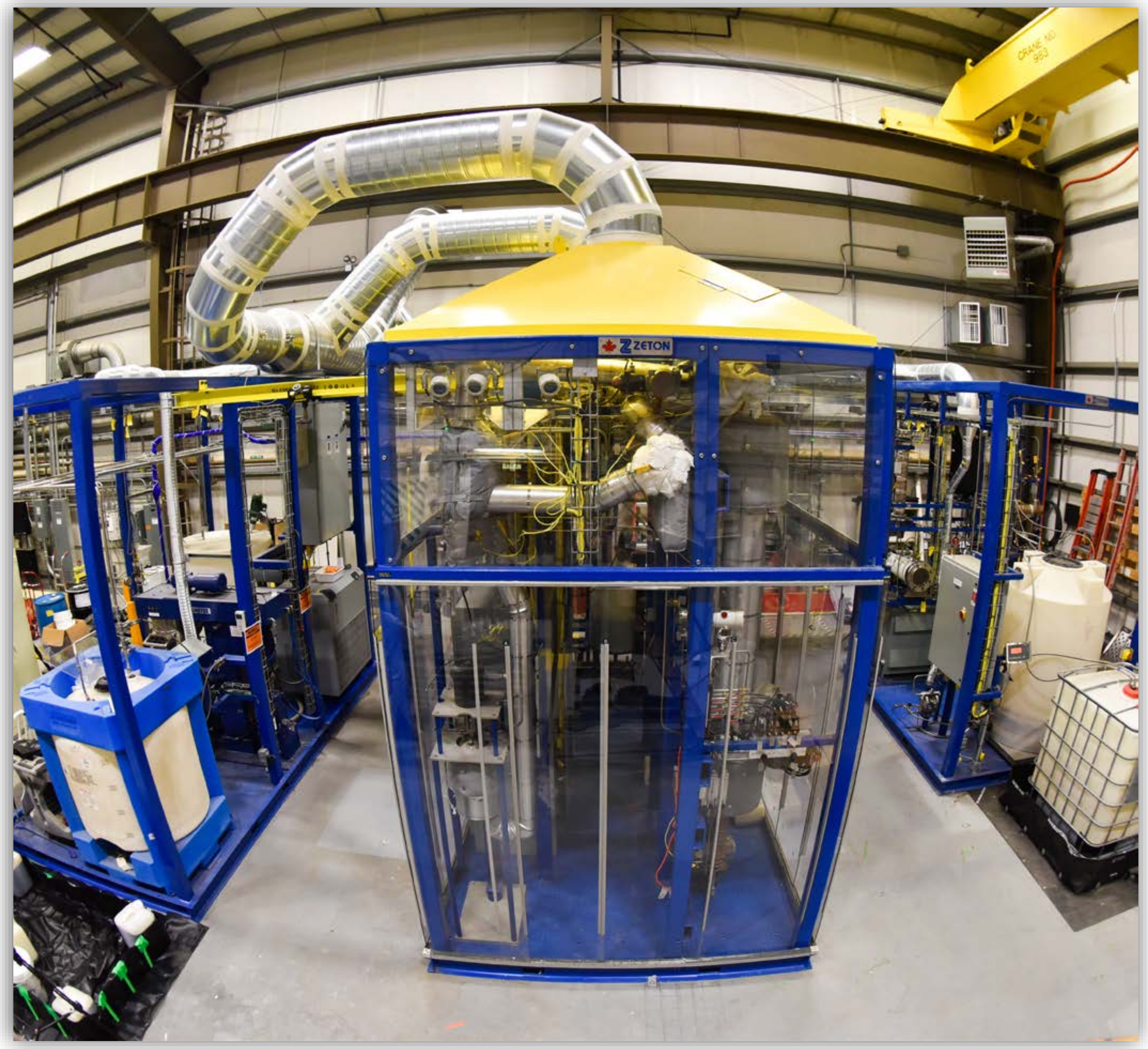
- Biocrude oil for fuels
- Ash for nutrient recovery
- Nitrogen recovery from aqueous phase

- Based on earlier work on **kelp** (Elliott et al. 2013), thermal pre-treatment improves **dewatering** and **pumpability** leading to higher yields
- Thus, algae HTL research in FY 2021 and beyond will focus on applying sequential HTL to macroalgae and turf scrubbers
- Optimization of fuel, starch and nutrient outputs informed by process modeling

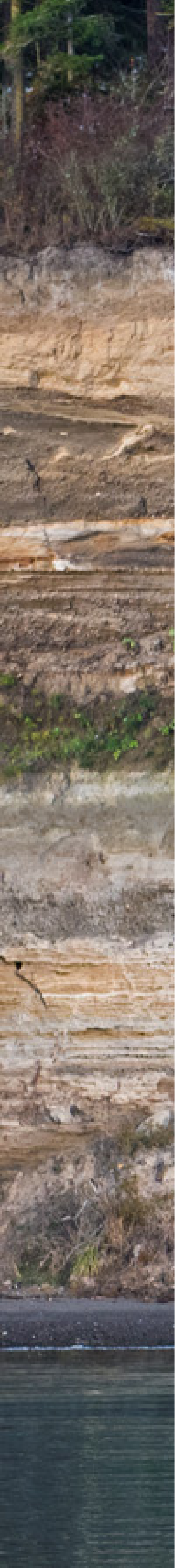
Pacific Northwest NATIONAL LABORATORY

Remaining barriers to commercialization

- Develop and demonstrate the following at pilot scale:
  - Robust solutions for aqueous phase treatment
  - Feedstock formatting and slurry pumping to high pressure; pressure let-down
  - Efficient heat exchange to reduce capital and operating expenses
  - Equipment for continuous separation of solid, oil, and aqueous phases
  - Long-term corrosion and material compatibility testing
- Pilot-scale systems have been fully designed and are nearing procurement and construction



PNNL’s engineering scale HTL system



Acknowledgements

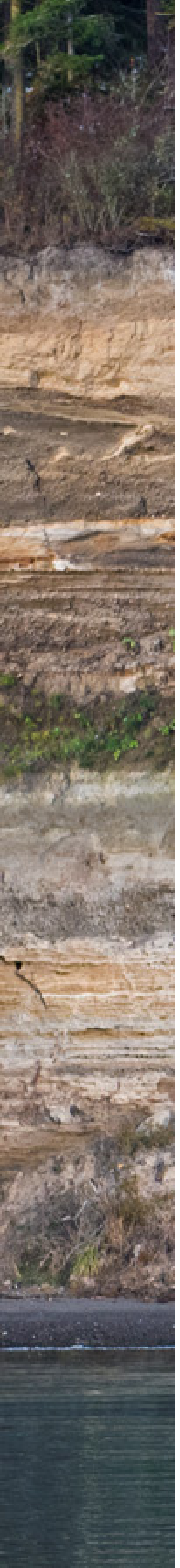
DOE Bioenergy Technologies Office (BETO)

- Dan Fishman, Technology Manager

PNNL Thermochemical Interface Team

- Dan Anderson, Project Manager
- Andy Schmidt
- Scott Edmundson
- Todd Hart
- Sam Fox
- Teresa Lemmon
- Heather Job
- Sue Jones
- Yunhua Zhu
- Rich Hallen

Pacific Northwest
NATIONAL LABORATORY



Thank you