# Whole Algae Hydrothermal Liquefaction Technology Pathway

Mary Biddy and Ryan Davis
*National Renewable Energy Laboratory*

Susanne Jones and Yunhua Zhu
*Pacific Northwest National Laboratory*

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National Renewable Energy Laboratory
15013 Denver West Parkway
Golden, Colorado 80401
303-275-3000 • www.nrel.gov

Pacific Northwest National Laboratory
P.O. Box 999
Richland, WA 99352
1-888-375-7665 • www.pnl.gov

# Whole Algae Hydrothermal Liquefaction

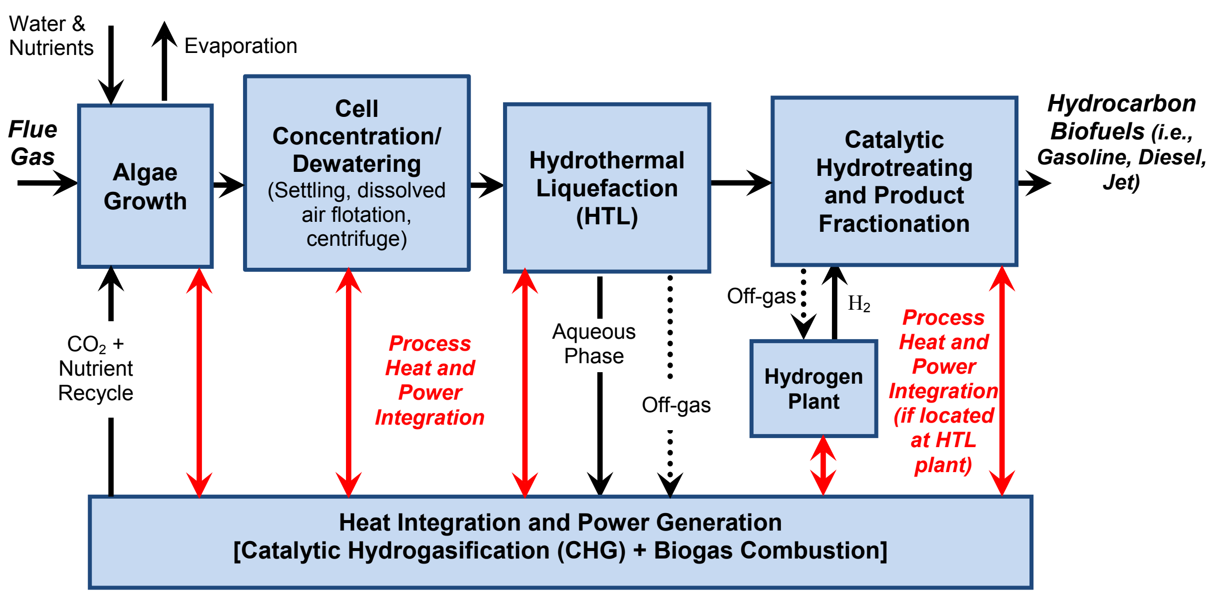
## Developing Technology Pathway Cases to Understand the Cost of Converting Biomass to Hydrocarbon Fuels

In support of the Bioenergy Technologies Office, the National Renewable Energy Laboratory (NREL) and the Pacific Northwest National Laboratory (PNNL) are undertaking studies of biomass conversion technologies to hydrocarbon fuels to identify barriers and target research toward reducing conversion costs.

Process designs and preliminary economic estimates for each of these pathway cases were developed using rigorous modeling tools (Aspen Plus and Chemcad). These analyses incorporated the best information available at the time of development, including data from recent pilot- and bench-scale demonstrations, collaborative industrial and academic partners, and published literature and patents. The economic results of these analyses are in the process of further refinement and will be published in FY13 and FY14 design reports. This report summarizes the preliminary technical data used for the models and identified data gaps.

This technology pathway case investigates the feasibility of using whole wet microalgae as a feedstock for conversion via hydrothermal liquefaction. Technical barriers and key research needs have been assessed in order for the hydrothermal liquefaction of microalgae to be competitive with petroleum-derived gasoline-, diesel-, and jet-range hydrocarbon blendstocks.

## Process Block Diagram (Co-Located Conversion and Hydrotreating Scenario)



## Key Highlights

- Microalgae grown via autotrophic pathways have the potential to make sizeable contributions to renewable fuel mandates, particularly due to their rapid growth rates and other favorable cultivation characteristics relative to terrestrial biomass feedstocks.
- An advantage of hydrothermal liquefaction (HTL) is that it uses the whole algae. Thus it is not necessary to promote lipid accumulation, nor is it necessary to extract the lipids.
- HTL is especially suited for conversion of wet feedstocks such as algae since the feed to the conversion unit is water based slurry. Thus no energy is expended for evaporative algae drying.
- For the algal HTL pathway, the overall economics for hydrocarbon biofuels are more strongly influenced by improvements in productivity rather than extractable lipid content.
- Hydrocarbon fuel can be produced by hydrotreating HTL oil under relatively mild conditions.
- Important research needs for this pathway include enhancing algal oil productivity on a sustained basis, optimizing the nutrient recycle, demonstrating wastewater treatment, and characterizing both HTL oil and hydrocarbon products.

## Process Design Details

***Wet whole algae source:*** The HTL plant is assumed to be co-located with algae production. The algal growth and cell concentration and dewatering steps are based on the Algal Lipid Upgrading (ALU) design (Davis et al. 2012), namely cultivation in open raceway ponds, steady-state harvesting of algal biomass at a rate equal to the biomass growth rate, and dewatering through a series of operations to concentrate the material to 20 wt% solids. Recycle of $CO_2$-containing HTL off-gas and HTL wastewater with dissolved ammonia to the algae ponds is also assumed.

***Hydrothermal liquefaction (HTL):*** Whole algal biomass slurry of ~20 wt% solids in water is pumped to the HTL reactor pressure of ~3,000 psia. Operating conditions and economics for the pumping system are based on experimental work from the National Alliance for Algal Biofuels and Bio-Products (NAABB) operating on wet whole algae and lipid extracted algae. Lab-scale experiments indicate that algal slurries are not difficult to pump (Zhu et al. 2013).

Whole wet algae at a 20 wt% solids content is hydrothermally treated in subcritical water, nominally 2,000–3,000 psia and 300°–350°C. The reaction temperature dictates the reactor pressure (e.g., the reactor pressure is sufficiently high to maintain water in the liquid state at the reaction conditions). The slurry entering the reactor is preheated by exchange with reactor effluent. During HTL of woody feedstocks, a buffering agent is employed to prevent formation of high molecular weight compounds (Zhu et al. 2012). Unlike HTL with wood, no buffering agent is needed when processing algae. This suggests that algae feedstocks produce a more stable HTL oil product than oil derived from processing wood. Algal nitrogen and sulfur partition between each phase to varying degrees.

The reactor effluent is a mixture of solids, liquids, and gas. Effective filtering is an important means of protecting downstream conversion catalysts. Further research is needed to identify the most effective means for doing so. The two liquid phases and the non-condensable gases are cooled and then separated. The non-condensable gases are sent to a steam boiler for power generation. The predominately organic liquid phase is sent to catalytic upgrading, and the predominately aqueous phase is sent to wastewater cleanup for carbon recovery. Solids removed by filtration might be recycled back to the algae ponds as nutrients.

There are a number of HTL studies in the literature, for example, Minowa et al. (1995), Brown et al. (2010), Duan and Savage (2011), Biller and Ross (2011), Jena et al. (2011), Valdez et al. (2011), Yu et al. (2011), Vardon et al. (2011), and Alba et al. (2012). However, these are all batch experiments with long residence times and variable operating conditions. Product recovery is typically by extraction. The scales, except for Jena et al. at 1,800 mL, are in the 35–75 mL range. Literature derived yields are in the 15–52 wt% range.

HTL experimental work at PNNL employs a continuous system with simple phase separation (no extraction systems). The scale is approximately 1 L, on the order of that used by Jena et al. (2011). HTL oil quality is very good, with expected ranges of 5%–10 wt% oxygen, 3–5 wt% nitrogen and yields of 45–55 wt% (all on a dry basis). The details of these runs, including element analysis will be reported in the Zhu paper (Zhu et al. 2013).

***Wastewater treatment:*** The nitrogen content in the wastewater (assumed to be dissolved ammonia) likely precludes the use of anaerobic digestion. Therefore, wastewater from the HTL process (and upgrading if it is co-located) is sent to a catalytic hydrothermal gasification (CHG) process to convert all organics to $CO_2$ and $CH_4$ similar to that described in Elliott et al. (2009). It is assumed that ammonia remains dissolved in the CHG wastewater. For CHG, the wastewater stream is pumped to ~3,000 psia, preheated to 370°C, then fed to a fixed bed catalytic reactor. Assumptions used in the model will be verified in FY13 by continuous lab-scale (1-liter fixed bed reactor) experiments using the aqueous phase derived from the aforementioned HTL reactions. Treated water should be recycled to the algae farm to reduce fresh nutrient demands during cultivation.

The produced CHG gas can be used to generate hydrogen if the HTL plant is co-located with the upgrading plant. If the HTL plant is not co-located with the upgrader, off-gas from the CHG system can be sent to a boiler to generate steam for process use.

***Steam and power:*** Superheated steam from the steam cycle boiler is used to power the process compressors. Depending upon the overall plant configuration, power demand in the conversion plant was balanced by either purchasing from or selling electricity to the grid. Future work will consider integration of algae production and harvest with the conversion plant.

***Product upgrading— catalytic hydrotreating:*** Algal HTL oil requires further catalytic processing to remove oxygen and nitrogen. Sulfur removal also occurs, but sulfur is present in the HTL oil to a much lower extent. The organic phase from HTL processing is catalytically hydrotreated to remove oxygen and nitrogen; the former is converted to $CO_2$ and water, while the latter is converted to ammonia. Sulfur is converted to hydrogen sulfide. The ammonia remains dissolved in the water phase, which in turn should be recycled to the algae farm assuming co-location.

Algal HTL oil requires milder upgrading conditions than fast pyrolysis oil, which requires 2-3 reactors in series, each operating at different temperatures and space velocities. Typical hydrotreating conditions are 250°–420°C, 1,000–2,000 psig, and 0.2–1.1 liquid hourly space velocity. Preliminary experimental work found that a single hydrotreater (continuous operation) was able to reduce the oxygen content to 1 wt% and the nitrogen content to <0.3 wt%. Short term testing showed no appearance of catalyst deactivation. Further optimization work will continue in FY13 to narrow the range of operating conditions.

The hydrotreater effluent is cooled to condense the produced water and hydrocarbons. The organic phase is fractionated into four boiling point cuts: $C_4$ minus, gasoline range, diesel range, and heavy oil range material. The heavy oil type material is assumed to be cracked in a conventional hydrocracker to produce additional gasoline- and diesel-range products. It is assumed that the product quality is sufficiently suitable for gasoline- and diesel-range blendstocks. Detailed product analysis has not yet been undertaken.

***Hydrogen plant:*** Hydrogen is assumed to be produced onsite. If the HTL plant is co-located with the upgrading facilities, off-gases from HTL and the hydrodeoxygenation section are sent to a conventional hydrogen plant consisting of a steam reformer, water gas shift reactor, pressure swing adsorption unit, and heat recovery. If the HTL plant is not co-located, then only the off-gases from hydrodeoxygenation are available for use in the hydrogen plant. The off-gases are mixed with enough supplemental natural gas to satisfy the hydrogen demand. No processing penalty is assumed for mixing off-gas with natural gas. The plant size is within typical commercial scale.

## Data Gaps, Uncertainties, and Research Needs

While the HTL oil production and hydrodeoxygenation (and de-nitrification) results are based on experimental data, the CHG wastewater processing model is literature based. Experimental results from FY13 tasks will be used to update the HTL, hydrotreating, and CHG portions of the model. The goal of this pathway is to reach a minimum fuel selling price of $3/gallon of gasoline equivalent (in 2011 U.S. dollars). To reach this targeted product price, the key bottlenecks, uncertainties, and areas for further development are summarized as follows:

- **Validate algae growth and oil productivity rates based on data from large scale demonstrations.** Previous work has demonstrated a strong economic sensitivity to lipid content and algal growth rate. Much of the existing data is based on literature values in controlled environments. It will be important to incorporate first-hand operational data on large-scale, outdoor, year-round operation to validate the assumptions and projections for these metrics.
- **Confirm design requirement of pond liners.** The costs for liners in algae cultivation exhibit the largest single-unit impact on overall economics and there is a great deal of uncertainty on their requirement. In reality, their use will depend on local soil characteristics, algal strain employed, and governing regulatory policies.
- **Reduce cost and increase efficiency of algae dewatering and concentration steps.** While the performance for dewatering operations is supported to a degree in literature (for operations utilizing wastewater dewatering technologies), such operations leave

room for further cost reduction if more cost-effective alternatives can be developed and proven at large scale.

- **Verify feed handling.** Feedstock handling is not anticipated to present issues because lab-scale experiments indicate that algal slurries are easier to pump than wood slurries and do not appear to have plugging issues. However, this will need to be definitively verified.
- **Understand effect of feedstock variability.** There are known compositional differences between strains of algae, and typically seasonal variations as well. The assumption that HTL yield and that of subsequent upgrading only affects product quality but not yield should be demonstrated. Preliminary tests in FY13 will address this, but additional research may be needed.
- **Assess nutrient recycle.** Future work must consider the impact and practical application of nutrient recycle on both the sustainability and economics of the process. Nutrient recycle has been identified as a key driver in meeting GHG reduction goals in the life cycle assessment of ALU. However, nothing is known about the actual practice, either as benefits (such as uptake of recycled nutrients) or as issues (such as accumulation of undesired compounds). This will involve a better understanding, for example, of the partitioning of nutrients, such as nitrogen and phosphorus, and non-nutrients among the various phases. Cultivation with real recycle also needs exploring.
- **Develop detailed reactor design and cost estimates.** A large high pressure reactor is required. The economic analysis for this system was based on hydrothermal liquefaction reactor experiments conducted within a continuously stirred tank reactor (CSTR). It is likely that a hybrid CSTR-plug flow reactor (PFR) would be much less expensive to scale up than a CSTR alone, and this will be investigated in the current fiscal year. Work is still needed to determine the most appropriate reactor(s) configuration that promotes full conversion and reduced capital costs.
- **Characterize feed and products.** Detailed characterizations of all the products and intermediates are needed. For example, better understanding of the quality of the HTL oil will help reveal the underlying HTL reactions and subsequent upgrading requirements. In addition to ultimate analysis, phase densities, gas analysis and whole oil distillation curves, analysis by GC-MS, HPLC, and $^{13}C$ NMR would be useful as the next step. Also needed is similar analysis on the major distillation fractions: gasoline range, diesel range, and gas oil range for the HTL oil and the hydrotreated oil. Understanding the speciation of alkenes, aromatics, and oxygenates, particularly as a function of processing conditions, will help manage hydrogen usage. Off-gas composition by GC is available from the HTL and hydrotreating experiments, but this may not be sufficient to assess the need for gas conditioning prior to use in a hydrogen plant. Detailed algal feed characterization is needed to assist determination of the trade-offs (if any) between lipid content and final product yield and quality, and the availability of recoverable nutrients. Lastly, testing for final fuel qualities, such as octane, cetane, and freeze, is desirable.
- **Optimize separations and carbon efficiency.** HTL oil and aqueous phase separation needs further work to recover more of the organic material into the HTL oil phase. Additionally, research is needed to understand the conversion of organics in the aqueous

phase to hydrogen, bio-products, and species that can rejoin the predominantly organic phase. Hydrocracking yields of the gas oil fraction should be demonstrated.

- **Demonstrate wastewater treatment.** Wastewater treatment is largely unexplored and anaerobic digestion is not considered appropriate for the types of species present. Catalytic hydrothermal gasification needs to be further explored to understand the impact of organic compounds on wastewater treatment, the toxicity of trace compounds, and the impact of ammonia in the conversion, and to minimize catalyst costs and carbon loss to wastewater treatment.
- **Improve catalyst performance.** Hydrotreating catalyst maintenance and stability are unknown, as are regeneration protocols and lifetimes. Longer-term testing with HTL oil and detailed characterization of catalyst performance and deactivation modes are needed. Parameter testing and development of compounds' structure-reactivity relationships is needed. There is a need to understand mass transfer issues of hydrogen in bio-oil and on catalyst.
- **Consider co-products.** Co-product opportunities have the potential to further lower the cost of hydrocarbon production from algal biomass and should be explored in future economic evaluations. The impact of any process modifications should be evaluated via a life cycle assessment as well, since the current algal models have been developed and integrated to ultimately achieve a sustainable process design. Key also for the production of co-products is to ensure that the volumes of co-products produced via these routes will not overwhelm the market demand.

## Summary and Next Steps

This study assessed the processing of whole algal biomass via conversion by hydrothermal liquefaction followed by upgrading and finishing to gasoline-, diesel-, and jet-range hydrocarbon blendstocks. A combination of preliminary experimental data and literature-based techno-economic analysis was performed to identify technology gaps, uncertainties, and research needed to achieve a minimum fuel selling price of $3/gallon of gasoline equivalent. A design case detailing this pathway will be developed by the end of FY13.

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