# Fractional Multistage Hydrothermal Liquefaction of Biomass and Catalytic Conversion into Hydrocarbons

## Virent Final Report for

**DOE Award Number: DE-EE0006286**

Lead Organization - Virent, Inc.

Subcontractors: Idaho National Laboratory

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# Executive Summary

The objective of this project was to develop an improved multistage process for the hydrothermal liquefaction (HTL) of biomass to serve as a new front-end, deconstruction process ideally suited to feed Virent's well-proven catalytic technology, which is already being scaled up. This process produced water soluble, partially de-oxygenated intermediates that are ideally suited for catalytic finishing to fungible distillate hydrocarbons.

Through this project, Virent, with its partners, demonstrated the conversion of pine wood chips to drop-in hydrocarbon distillate fuels using a multi-stage fractional conversion system that is integrated with Virent's BioForming® process. The majority of work was in the liquefaction task and included temperature scoping, solvent optimization, and separations.

The project work included preprocessing and liquefaction at lab scale and further applied research integrating catalytic processing, final product polishing and quality testing. At the completion of the project, the Technology Readiness Level (TRL) advanced from TRL-1 to TRL-3. Despite the advancement to TRL-3, there were technological challenges at lab scale that were encountered in the project which resulted in unexpected low yields of soluble carbon from the hydrothermal liquefaction. As a result, project milestones of advancing the technology from TRL-3 to TRL-4 were not fully met over the course of the first budget period. Plans were made to revisit the milestones from TRL-3 in the second budget period, but an agreement of mutual termination ended the project prior to the initiation of budget period 2.

Major accomplishments of the project included:

- Production of liquid fuels products from loblolly pine feedstock
- Construction of a lab-scale flow-through hydrothermal liquefaction pilot plant unit capable of generating hydrolysates from biomass feedstock
- Integration of liquefaction products into Virent's BioForming® process
- Optimization of corn stover pretreatment based on reduction of ash content and retention of carbon in the stover

Several challenges were identified that, once solved, would further improve overall yields and reduce costs. These challenges include the need for:

- Optimization of liquefaction steps to maximize carbon yields and minimize cost
- Improved utilization of lignin through product stabilization and optimized catalytic upgrading
- Integration of downstream catalytic upgrading with liquefaction to reduce raw materials needs and improve yields

Experimental work for this DOE funded project started in October 2013 and was completed in March 2016. An integrated lab-scale biomass to distillate fuels process was designed, built, and operated to demonstrate feasibility of a hydrothermal liquefaction front end for the BioForming process within this project. Data collected from this integrated process was used to establish a baseline yield and production cost estimate for the process. Significant technical improvements in operability, yields, and economics of this technology were identified. The cumulative effects of these improvements could result in significant yield increases which would lower overall cost estimates.

### *Project Background and Approach*

The objective of this project was to develop an improved multistage process for the hydrothermal liquefaction (HTL) of biomass to serve as a new front-end, deconstruction process ideally suited to feed Virent's catalytic technology that is well-proven and already being scaled up. This process produced water soluble, partially de-oxygenated intermediates that are ideally suited for catalytic finishing to fungible distillate hydrocarbons. Targeted stage-wise liquefaction with inter-stage separation was applied in a novel approach to selectively solubilize, partially deoxygenate and then recover the major biomass components. Those recovered soluble oxygenate fractions then underwent catalytic finishing to hydrocarbons via Virent's novel BioForming® platform technology.

The major objectives of this project were to:

- Develop a new HTL deconstruction system that will significantly **improve overall carbon efficiency** (primary barrier objective) by improving the carbon yield for each of the major classes of biomass components.
- Use reaction chemistries, solvents, process conditions, reactor types and system configurations that lead to significantly improved carbon efficiency.
- Create and demonstrate deconstructed intermediates that serve as advantaged feedstock for catalytic finishing because they can be **readily separated from the process**, have already been partially deoxygenated, and are either soluble in aqueous phase or oil phases and can be fed forward to catalytic finishing.
- Investigate **selective separation technologies** specific to process conditions in this multistage HTL process.
- Integrate the improved HTL process with Virent's BioForming® process.
- Demonstrate the generation and utility of biomass-derived, in-situ, **hydrogen-donor solvents** that may assist in hydrogen transfer.
- Demonstrate the production of distillate-range products from the oxygenated advantaged intermediates derived from the fractional multistage HTL of biomass.
- Investigate mechanical and chemical pre-processing options for upgrading stover quality to the same or better quality as white wood to demonstrate the viability of both **high impact feedstocks**.

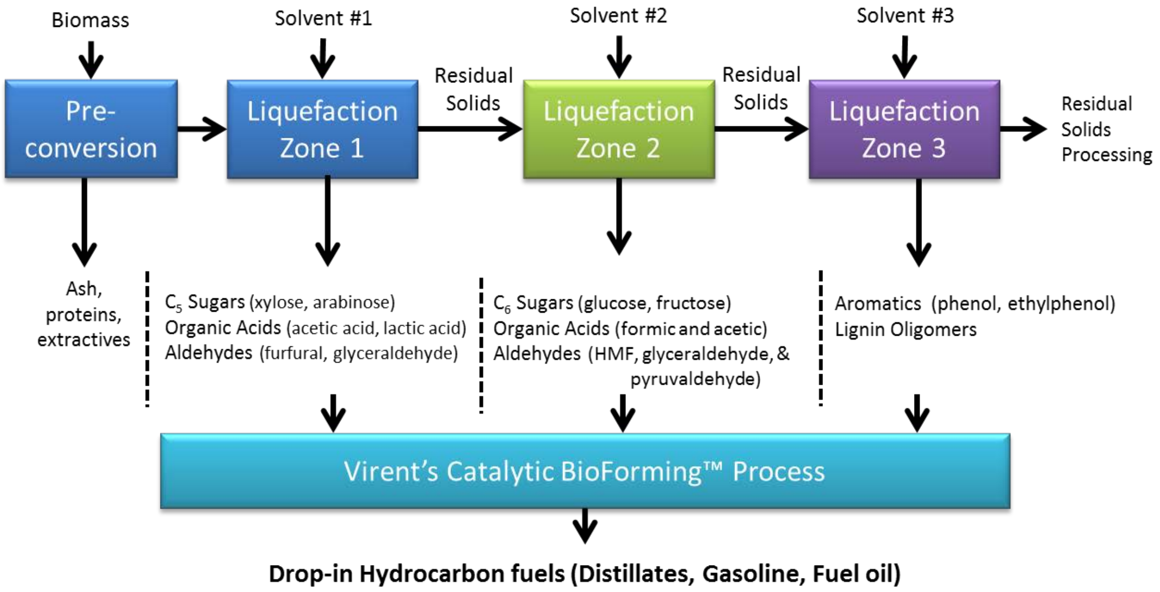

**Figure 1. Virent's Liquefaction of Biomass – Fractional multistage hydrothermal liquefaction of biomass using selective fractionation and separation of soluble oxygenated intermediates for catalytic upgrading.** *Note: Solvent streams may include but are not limited to: water, dilute acids, ketones, alcohols, phenols, etc., many of which are derived from recycled, in-process liquid streams. Example products from each zone are taken from the literature. [1]*

The Project investigated two high-impact biomass feedstocks. Debarked loblolly pine wood chips were used to develop a benchmark process. Corn stover was the second feedstock and it was mechanically and chemically pre-processed by Idaho National Laboratory to more closely match the ash content found in pine chips.

Virent's BioForming technology efficiently converted oxygenated biomass components into fungible distillate-range hydrocarbon products. Hydrothermal liquefaction of biomass using selective, stage-wise fractionation and separation was to be investigated. In this approach, the deconstruction reaction conditions were controlled for each class of biomass components (e.g.: hemicellulose, cellulose or lignin) to improve yield of the respective reaction products and facilitate separation to maximize overall carbon recovery. Practicing targeted, stage-wise HTL with interstage separation minimized the formation of non-functional degradation products (including light gases and char) and maximized the yield of useful oxygenated intermediates available for catalytic conversion thereby increasing the carbon efficiency of the overall conversion of biomass to distillate product.

This overall approach alleviated several typical constraints identified in the three Technical Barrier Areas. For example, it increased the carbon efficiency because high concentrations of soluble components in the aqueous phase are desirable (Barrier 1) and the water was easily separated later once hydrocarbons are formed (Barrier 1 and 3). It increased carbon yield through use of external hydrogen to efficiently convert biomass carbon to liquid hydrocarbon fuel. The combined process generated hydrogen donor solvents (in-situ and recycled from elsewhere in the process, cited in Barrier 2) that could be used in a selective portion of the process enabling smaller equipment sizing and more targeted use of hydrogen. The separation challenges may be better managed by avoiding char formation, utilization of interstage hot solid/liquid separation systems to avoid undesired hard to separate condensation products, and decreasing the required biomass throughput with each successive stage which may decrease equipment costs (Barrier 3). Lastly, the back-end catalytic conversion process produced proven, quality hydrocarbon products that do not need further processing which often can lead to further yield loss, (Barrier 1).

### *Project Milestones and Deliverables*

Milestones were established and monitored throughout the project to ensure coordination and alignment. Key milestones, performance metrics and deliverables are included in Table 1.

**Table 1: Milestones and Deliverables**

| Milestone Title | Description / Metric | Deliverable |
|---|---|---|
| TRL-2 Applied Research. Demonstrated carbon efficiency. | *Demonstrate carbon efficiency of >60% for HTL from biomass to soluble carbon in batch tube experiments.* | Report Carbon efficiency in report. |
| Complete Liquefaction Prototype skid construction | Complete construction of the prototype liquefaction skid | Prototype Liquefaction Skid |
| TRL-3 Proof of Concept Demonstrated carbon efficiency. | *Demonstrate carbon efficiency >70% for HTL to intermediates and >50% overall.* | Report Carbon efficiency in the TEA/LCA report |
| TEA and LCA | Complete intermediate TEA and LCA on the process configuration | TEA/LCA Report |
| Stage Gate Review | Hold Stage Gate review to assess TRL-3 status and determine if the project should proceed to TRL-4 | Go/No-Go Decision |
| TRL-4 Preliminary Integration. Demonstrated carbon efficiency. | *Demonstrate carbon efficiency of >60% overall.* | Report Carbon efficiency in the Final Report. |
| Demonstrate Integrated Prototype Operation | Virtually couple Liquefaction unit with BioForming to produce distillate product for evaluation. | Up to 1L distillate sample |
| Final TEA and LCA | Complete TEA and LCA on the final process configuration. | TEA and LCA Report for Budget Period 2 |
| Project Reporting | Summarize technical findings for TRL-2, TRL-3, and TRL-4 | Technical and Financial reports for TRL-2, TRL-3, and TRL-4 |

### *Project Summary and Major Accomplishments*

The objective of this project was to develop an improved multistage process for the hydrothermal liquefaction (HTL) of biomass to serve as a new front-end, deconstruction process ideally suited to feed Virent's catalytic technology that is well-proven and already being scaled up. Additionally, the project investigated loblolly pine and pretreated corn stover as potential HTL feedstocks. The project was broken down into eight major tasks:

1. **Stover Preconversion Performance Target - Idaho National Laboratory and Virent**
   Overall, this work consists of a two-step process to reduce the ash load from corn stover from 12.6wt% to less than 1% while maintaining 90% of carbon conservation. The ash components can poison catalysts in the downstream catalytic upgrading steps, so removal of the ash is important. For comparison, the loblolly pine used for the other five milestones of the project contains only 0.4wt% ash. INL has completed the first step of the process which has reduced the overall ash to ~2% with losses of ~40% of the carbon to the black liquor. In order to meet the 90% recovery of carbon the material must be reincorporated into the Virent HTL process. Virent received samples of the material from INL from the first stage and INL for evaluation.

2. **TRL-2 Liquefaction Performance Target – Virent**
   This milestone consisted of demonstrating a carbon efficiency of >60% of carbon from loblolly pine to soluble carbon hydrolysate in batch experimentation. Virent demonstrated >70% carbon solubilized to liquid with a two-step process early in calendar year 2015.

3. **TRL-2 Catalytic Upgrading Performance Target – Virent**
   This milestone consisted of demonstrating >65% carbon yield to liquid fuel products with model feeds of hydrolysate across the Virent distillate platform. Virent demonstrated an average of >75% carbon yield to liquid fuel products over the course of ten days of continuous operation with a model feedstock which included model components for solubilized hemicellulose, cellulose, and lignin.

4. **TRL-3 Liquefaction Performance Target – Virent**
   This milestone consisted of demonstrating a carbon efficiency of >70% from loblolly pine to soluble carbon hydrolysate. This milestone, in moving to TRL-3, required the construction of a slurry based HTL pilot system. The system was designed in the second half of 2014 and built during the first half of 2015. The system completed commissioning in August of 2015. Overall carbon recovery of biomass to soluble carbon hydrolysate was 55%. It was expected that overcoming certain operational limitations would allow for greater overall carbon recovery from biomass.

5. **TRL-3 Catalytic Upgrading Performance Target-Virent**
   This milestone consisted of demonstrating >70% carbon yield to liquid fuel products with biomass hydrolysates across the Virent distillate platform, with a >50% carbon yield cumulatively from biomass to liquid hydrocarbon products (70%*70% = 49%). Total overall carbon recovery from biomass to liquid hydrocarbon products was 34%.

6. **TRL-3 TEA and LCA – Virent**
   This milestone consisted of completing an intermediate Techno-Economic Assessment (TEA) and Life Cycle Assessment (LCA) on the process configuration and demonstrate >60% Greenhouse Gas (GHG) reduction. Overall, with the associated modeling assumptions, the demonstrated performance of the process was estimated. GHG reductions were also estimated to be greater than 60%. The largest sensitivities to the LCA are $H_2$ consumption and electricity

export, and by focusing on these areas we believe the high end of the range of GHG reduction is feasible.

7. **TRL-4 Preliminary Integration – Virent**
   No work was completed toward TRL-4. A decision to mutually terminate the project was made prior to any work in TRL-4 being initiated.

8. **Project Management**

   At the start of the project, a comprehensive Project Management Plan was assembled. Quarterly reports were prepared along with regular contact with the DOE project officer. During periods of high project activity, monthly project calls were held. A go/no-go stage-gate review was conducted in 2016. The decision was made to continue the project with an updated scope and commensurate cost category revisions. A mutual termination agreement was completed in March 2017 that ended the project after Q2 2017 with no additional experimental work completed after the stage gate in 2016.

### Summary of Results

This project utilized hydrothermal liquefaction to solubilize the primary carbon-containing fractions of loblolly pine (hemicellulose, cellulose, and lignin) and demonstrated the integration of the hydrothermal liquefaction technology with Virent's BioForming process to generate high-quality distillate range fuels. An integrated lab-scale biomass to distillate fuels process was designed, built, and operated to demonstrate feasibility of a hydrothermal liquefaction front end for the BioForming process within this project. Data collected from this integrated process was used to complete a techno-economic analysis and life-cycle analysis, as well as to establish a baseline yield and a cash cost estimate.

## Feedstock

### Executive Summary

Ash in biofuel feedstock can adversely affect feedstock handling and conversion processes. Ash concentrations in biomass are highly variable and can range from less than 1 wt% in clean wood chips, to over 20 wt% herbaceous crop residues such as multi-pass corn stover. The goal for Idaho National Laboratory (INL) in this project was to remove silicon, phosphorus, sulfur and alkali and alkaline earth metals (AAEMs) from corn stover to enable its use in Virent's hydrothermal liquefaction and catalytic BioForming® process with yields as white wood. To this end, INL has tested sequential alkaline preprocessing and extraction (removal of structural ash components) and dilute acid leaching (removal of AAEMs) on multi-pass corn stover.

Screening for the best alkaline preprocessing conditions was performed over a range of incubation times, temperatures and solids loadings using INL's Chemical Preconversion System. The conditions selected for subsequent tests that incorporated a dilute acid leaching step were: 60 minutes, 180°C and 50 wt% solids. A 1:10 wt% NaOH to corn stover loading was used for all tests. Each alkaline preprocessing step was followed by an alkaline extraction in a bench top reactor using 10 wt% solids and 1 wt% NaOH at 90°C for 24 hours. The purpose of this step was to extract organics and inorganics liberated during the alkaline preprocessing. Finally, the remaining solids were harvested and a dilute acid leach was performed for 24 hours at 10 wt% solids and various temperatures and acid loadings. When applied sequentially to the alkaline preprocessing and extraction, the most severe dilute acid leach conditions tested (90°C and 1 wt% $H_2SO_4$) resulted in the removal of 91.8 wt% of the total ash and 49.7 wt% of the initial organic material. This resulted in a final ash content of 1.03 wt%. At these conditions, 90.2, 82.7, 96.7, 98.1, 98.2, 98.9 mol% of the silicon, sulfur, phosphorus, calcium, potassium, magnesium was removed.

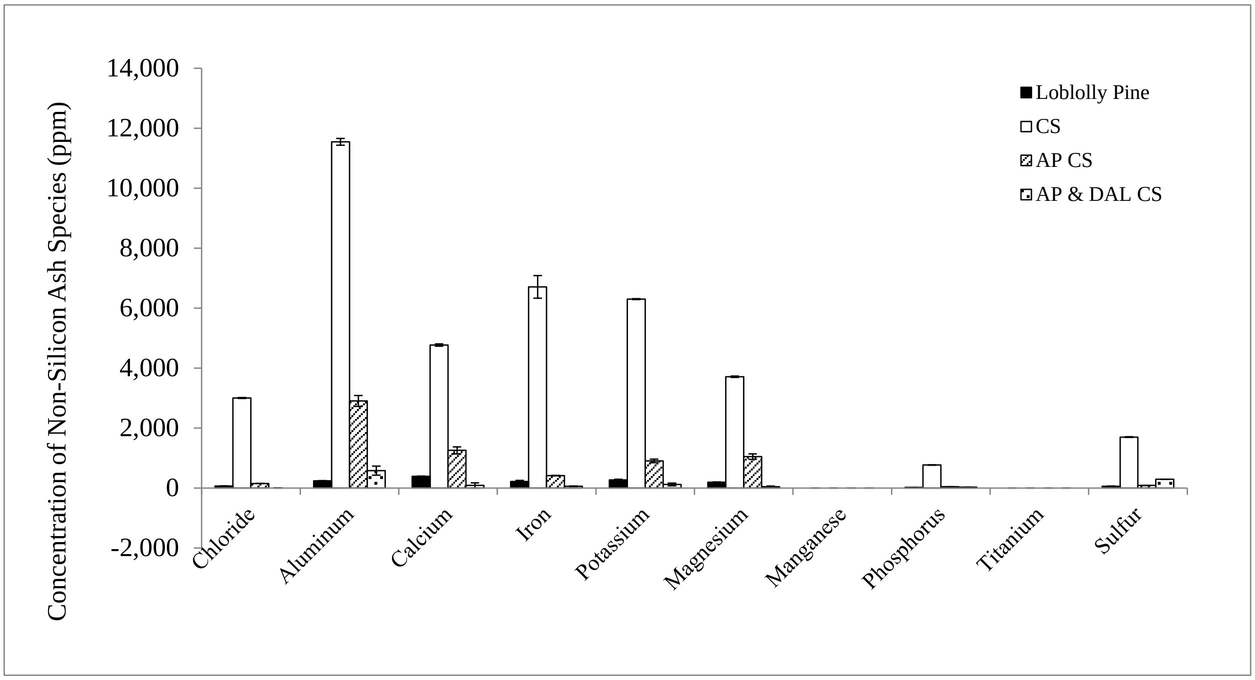

**Figure 2: Comparison of non-silicon ash species content in loblolly pine (LP), multi-pass corn stover (CS), alkaline preprocessed and extracted corn stover (AP CS) and alkaline preprocessed, extracted and dilute acid leached corn stover (AP & DAL CS).**

# TRL-2: Applied Research

## TRL-2: Hydrothermal Liquefaction

A demonstrated multistage carbon efficiency of 60% in batch experiments was required to meet the TRL-2 hydrothermal liquefaction milestone. The batch reactor experimental apparatus used to meet this milestone was capable of rapid heating and cooling and was capable of withstanding pressures and temperatures that kept solvents in the liquid phase. Residence times were relatively long compared to expected requirements of a flow-through design. At the conclusion of the experiment, solids and liquids are separated and appropriately analyzed.

Prior to executing experiments intended to meet the TRL-2 HTL milestone, a series of solvent scoping experiments using loblolly pine were completed in a similar batch-style experiment set to assess the capability of different solvent/temperature combinations to extract hemicellulose, cellulose, and lignin (Figure 3). 20-30 different solvents were used that ranged from oxygenates to acids and bases, and were able to solubilize all three major carbon-containing biomass components. The results of these experiments largely formed the basis for the lineup used to meet the TRL-2 HTL milestone.

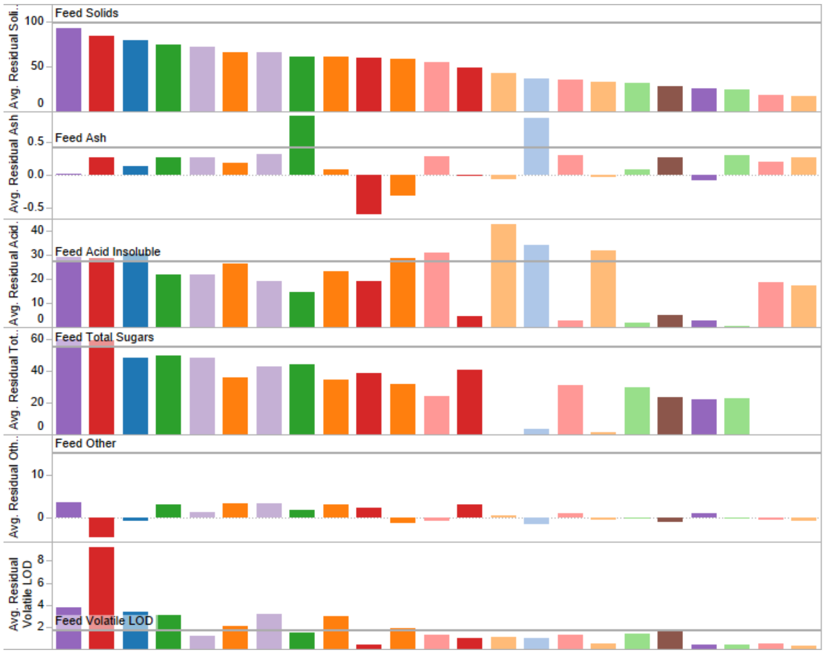

**Figure 3: Biomass characterization results of solvent screening experiments**

The multistage HTL lineup chosen solubilized greater than 70% of the carbon to liquid product intermediates, with less than 30% of the carbon remaining in the residual solids (Figure 4). Hemicellulose, cellulose, and lignin were all solubilized by the multistage process.

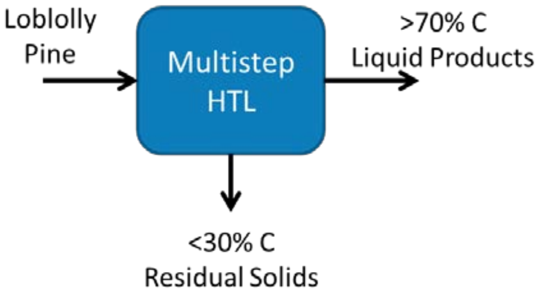

**Figure 4: TRL-2 Multistage HTL PFD**

## TRL-2: BioForming Catalytic Upgrading

A carbon efficiency of greater than 65% in the BioForming catalytic upgrading of model hydrothermal liquefaction intermediates was required to meet a second TRL-2 milestone. The BioForming process is an existing 3-stage catalytic process that had been developed by Virent to produce “direct replacement” liquid fuels from biomass-derived feedstocks. This particular variation of the process targeted the production of distillate-range fuels from loblolly pine. Model hemicellulose, cellulose, and lignin molecules were chosen for upgrading and fed to the appropriate step in the BioForming process. A hydrogen cofeed was required to upgrade the model feed to fungible liquid fuels. Total yield of carbon through catalytic upgrading was >75% (Figure 5). The oxygen content of the final product was in line with that of a typical distillate fuel stream.

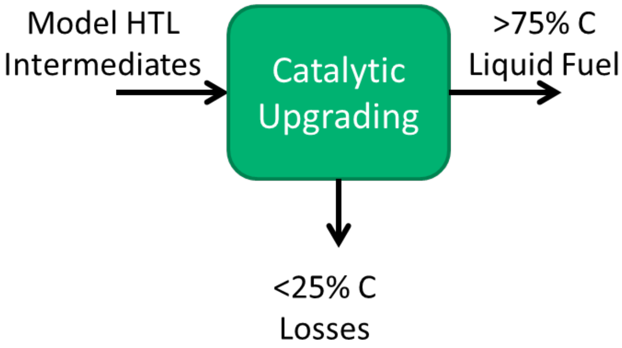

**Figure 5: TRL-2 Catalytic Upgrading PFD**

# TRL-3: Proof of Concept

## TRL-3: Hydrothermal Liquefaction Flow-through Unit (PP29)

A picture of the flow-through hydrothermal liquefaction unit designed and constructed under this project (henceforth referred to as PP29) is shown on the following page (Figure **6**). PP29 is divided into four subsystems: the feed system (slurry mixing tank and feed pump), the hydrothermal liquefaction reactors (large and small), the cooling system and the solid liquid separation system. All phases of PP29 run continuously, except the solid liquid separation system. It completes only one stage of a multistage HTL process at a time.

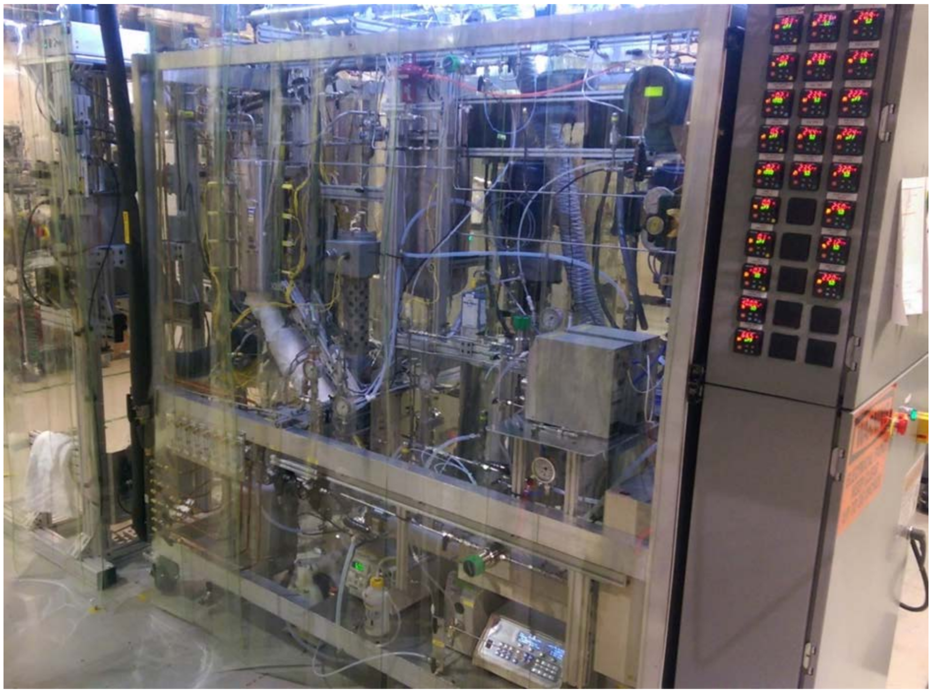

**Figure** 6**: Flow-through Hydrothermal Liquefaction Unit (PP29)**

## TRL-3: Hydrothermal Liquefaction

Prior to any liquefaction work, commissioning tests in the form of conditions scoping was performed in PP29 to verify the system performed as designed. These tests confirmed the system was capable of achieving the range of conditions the unit was designed to accommodate (Table 2).

**Table 2: PP29 Commissioning Test Conditions**

| **Unit Op** | **HTL** |
|---|---|
| **Temperature** | 20-300°C |
| **Rx Pressure** | 0-1500 psig |
| **Residence Time** | 0-10 min |
| **Test Liquid** | Water |

Upon completion of commissioning tests, a multistage HTL approach was defined and experiments designed to execute the approach. The target of the approach was the TRL-3 milestone of 70% carbon recovery of the biomass into liquid intermediates. These intermediates would then be fed into the BioForming process for upgrading to liquid fuels.

Each stage required a scoping and production run. The scoping run defined the best set of conditions to run the production run at based on maximizing yield and minimizing carbon losses. The production run focused on running the liquefaction unit at the defined conditions to generate hydrolysate material for catalytic upgrading and residual solids for scoping and production runs of subsequent liquefaction stages. The bulk of the challenge in these steps was keeping PP29 running; many failures were encountered including fouling, bridging, solids settling out, etc. The result was a reduction in the temperature/residence time space compared to the original design criteria (Figure 7).

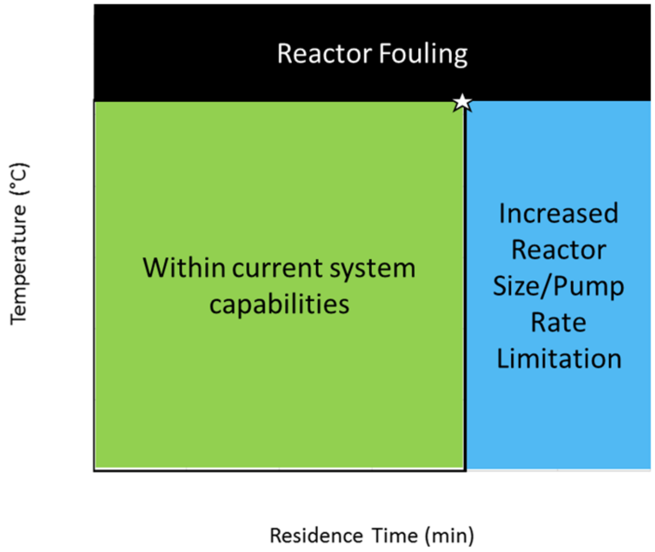

**Figure 7: Reduction in experimental space due to operational issues**

The final process lineup consisted of three stages. These three stages solubilized primarily the hemicellulose and cellulose fractions of the biomass, with limited solubilization of lignin. The first two stages were completed using the hydrothermal liquefaction flow-through unit. Stage 1 focused on solubilizing most of the hemicellulose in the biomass. In that stage, ~24% of the carbon was solubilized, as shown in Figure 8. The stage 1 production run was completed with a total of thirteen weight checks over 5 weeks. Mass and carbon solubilized for each of those thirteen WCs is shown in Figure 9.

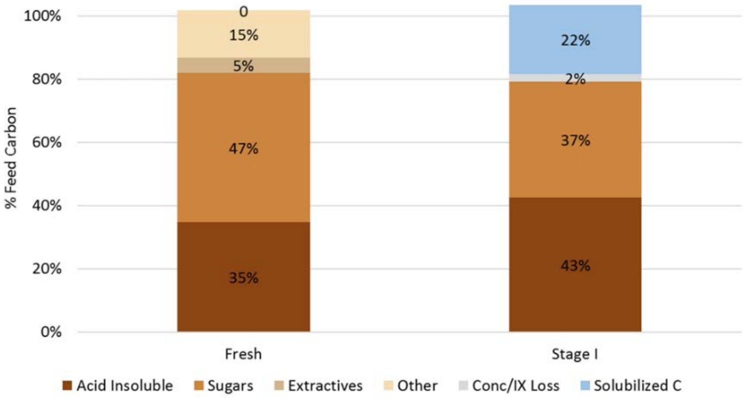

**Figure 8: TRL-3 HTL Stage 1 Carbon Summary**

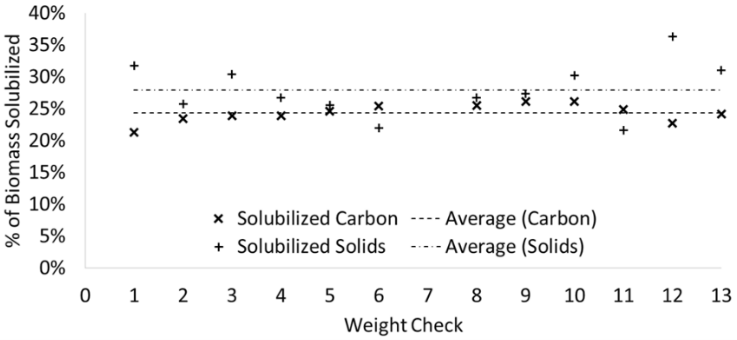

**Figure 9: TRL-3 Stage 1 Production Run Mass and Carbon Solubilized**

Stage 2 focused on solubilizing the remaining hemicellulose and as much cellulose as was possible. Due to the aforementioned conditions limitations, stage 2 was only able to solubilize an additional 12% of the carbon, leaving about 25% of the biomass carbon as cellulose (Figure 10). The stage 2 production run was completed over one week and five weight checks. Mass and carbon solubilized in each of those five WCs is shown in Figure 11.

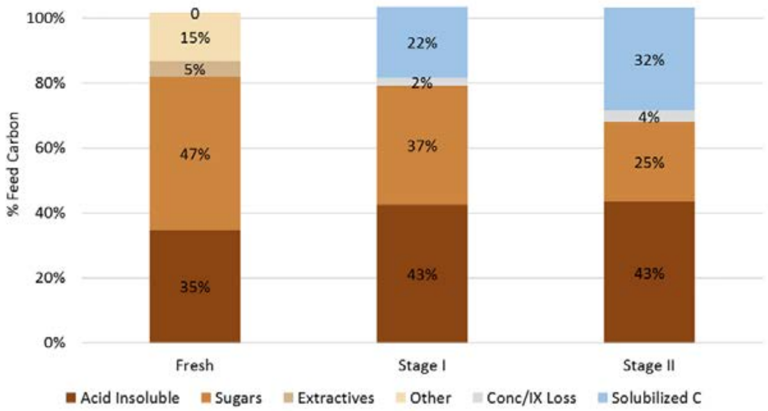

**Figure 10: TRL-3 HTL Stages 1 and 2 Carbon Summary**

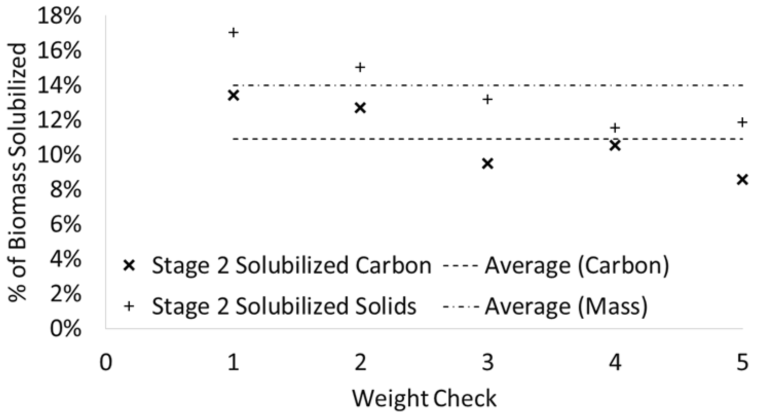

**Figure 11: TRL-3 HTL Stage 2 Production Run Mass and Carbon Solubilized**

Stage 3 targeted the removal of the remaining cellulose left from stage 2. It was completed in a batch reactor capable of longer residence times and utilized a catalyst and hydrogen to react the solubilized biomass in-situ. The result of this stage was a product profile similar to an intermediate stream in the BioForming process, and was deemed suitable for catalytic upgrading (Figure 12). An additional 25% of the biomass feed carbon was solubilized in stage 3 (Figure 13). The overall carbon recovery of these three stages to liquid phase intermediates was 61%.

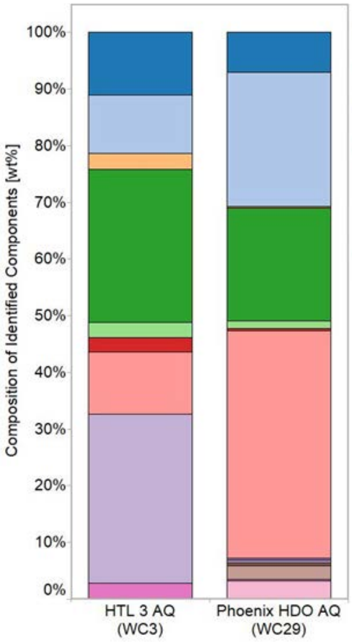

Figure 12: TRL-3 Stage 3 Aqueous Product Comparison with Phoenix

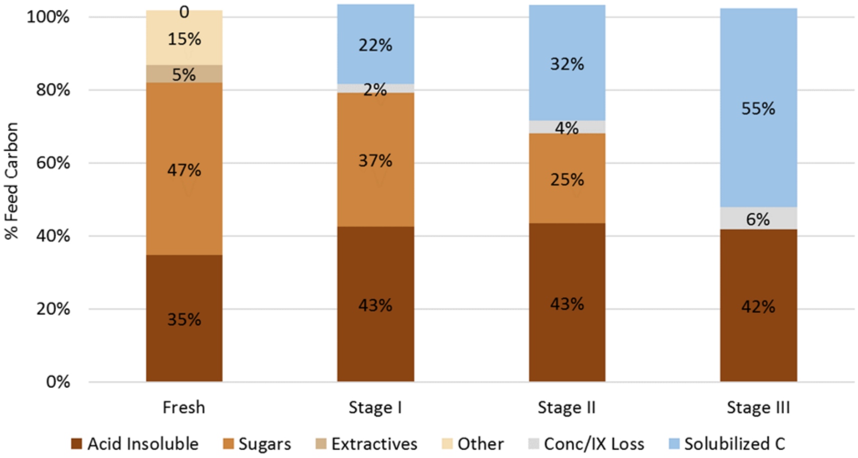

Figure 13: TRL-3 HTL Stages 1-3 Carbon Summary

Products from HTL stage 1 and stage 2 required concentration and ash removal prior to being suitable to feed to the BioForming process (Figure 14). Products from these two stages were concentrated separately using an on-site rotovap unit. The concentrated product was polished using a mixed-bed ion exchange resin. The resulting products retained 90% of the carbon, and were adequately prepared for catalytic upgrading. The carbon losses due to product upgrading were included in the overall liquefaction yield, resulting in a total yield of carbon from biomass to solubilized liquid intermediates of 55%, as shown in Figure 15.

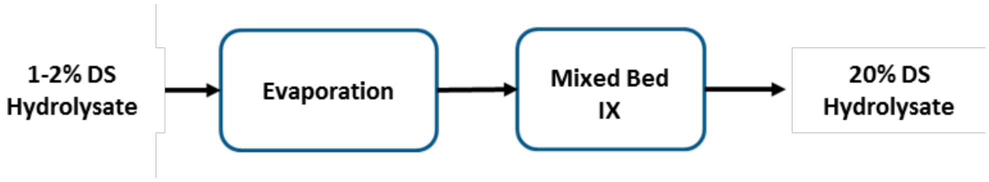

Figure 14: HTL Product Upgrading PFD

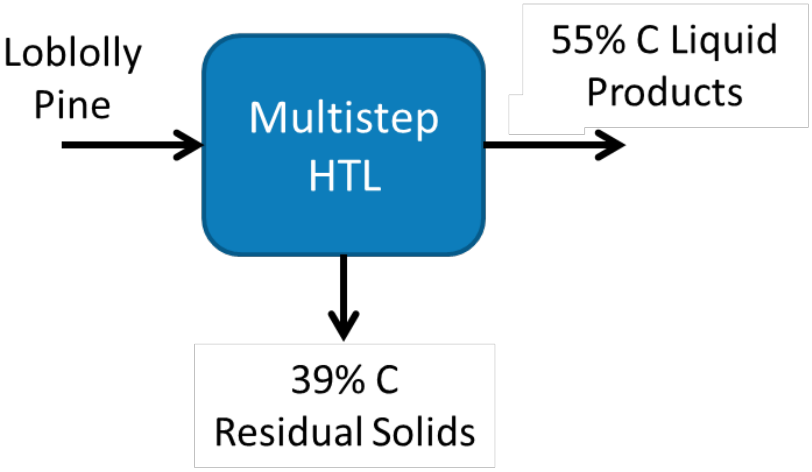

Figure 15: TRL-3 Multistage HTL PFD

## TRL-3: BioForming Catalytic Upgrading of HTL Products

A carbon efficiency of greater than 70% in the BioForming catalytic upgrading of hydrothermal liquefaction intermediates was required to meet a second TRL-3 milestone, and the overall TRL-3 milestone of greater than 50% recovery of biomass carbon to finished liquid fuel products. The process lineup for this step was identical to that used in TRL-2, except the finished hydrolysate from TRL-3 HTL was used as feedstock.

The feedstock was a mixture of hydrolysates from stage 1 and stage 2. The mixture ratio was dependent on the percent conversion of biomass by weight in each stage. Liquid product from HTL stage 3 was not fed to the BioForming process due to limited quantity of the material, however the analytical makeup indicated that the material would make a suitable intermediate stream in the BioForming process, and, thus, the carbon associated with stage 3 was included in the total overall yield structure.

Total carbon recovery of HTL products to liquid fuels of the BioForming catalytic upgrading process was 62% (Figure 16). The overall carbon yield from biomass to finished liquid fuel products was 34% (Figure 17). An overall carbon summary of HTL and catalytic upgrading in TRL-3 is presented in Figure 18.

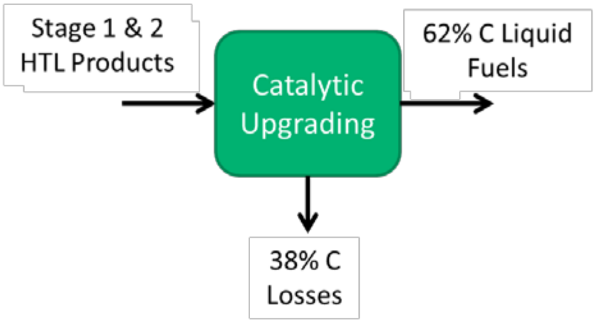

Figure 16: TRL-3 Catalytic Upgrading PFD

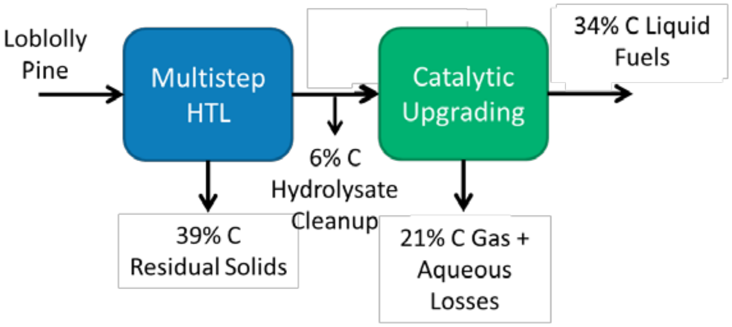

Figure 17: TRL-3 HTL + Catalytic Upgrading PFD

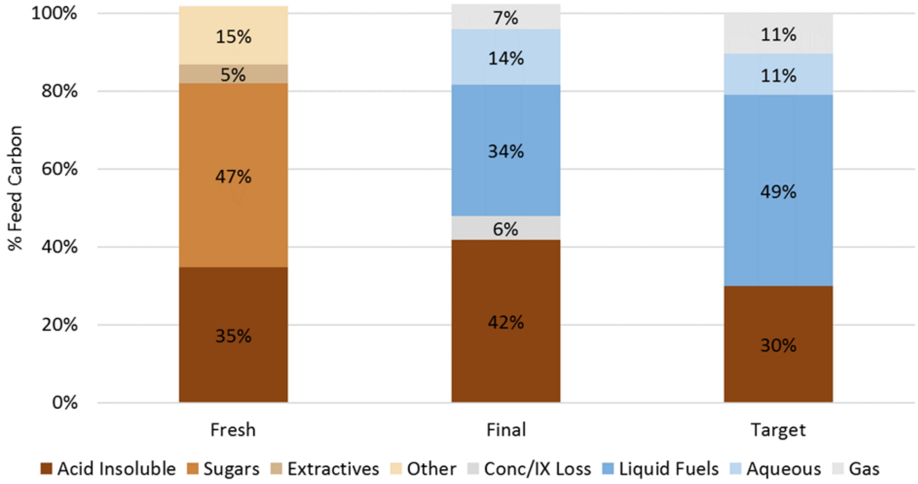

Figure 18: TRL-3 HTL + Catalytic Upgrading Carbon Summary

# Techno-economic and Life Cycle Analysis

## Commercial Model

An integrated process model was created as part of the project to evaluate the expected process at a commercial scale of 2,000 dry MT loblolly pine input per day. This section describes the process design for the conversion of lignocellulosic biomass to advanced biofuels. The model incorporated all aspects of a commercial process from feedstock through final hydrocarbon products, as well as OSBL unit operations such as utilities and boiler/turbogenerator.

Process conditions and reported yields/results were based on experimentally derived data. All costs were projected in 2014 dollars. The next sections briefly describe the major process operations.

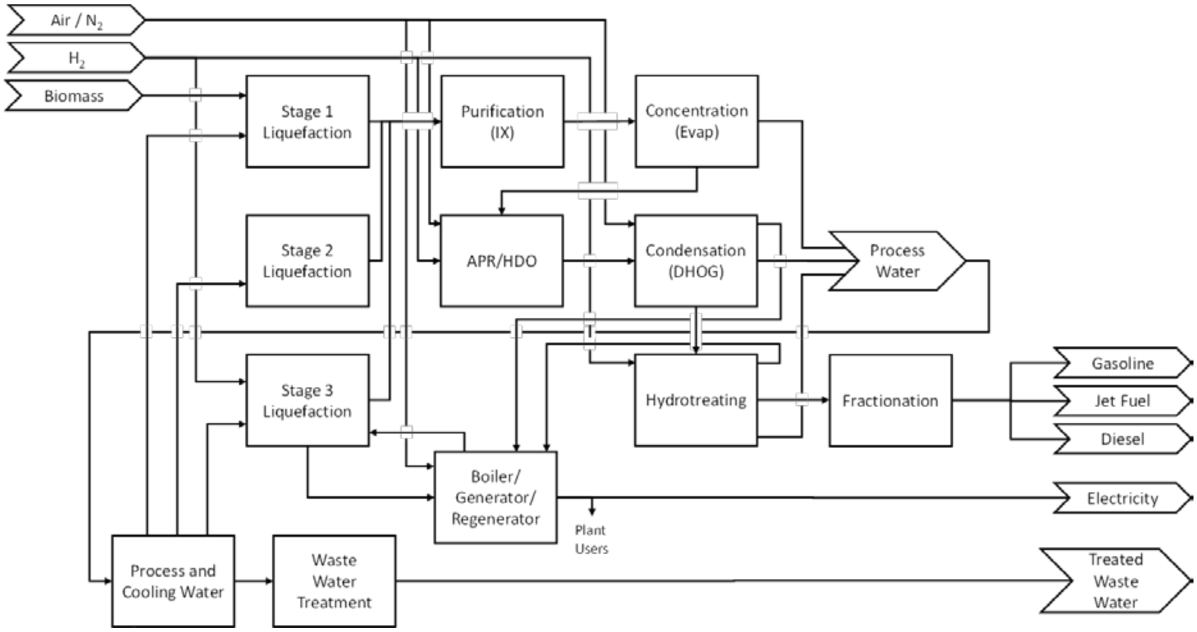

**Figure 19: Final configuration PFD for converting biomass into final hydrocarbon products.**

### *Liquefaction*

The milled biomass is pumped into the reactor for stage 1 Liquefaction, where it is mixed with hot liquid solvent at elevated pressure. A portion of the biomass is solubilized in this first stage and removed with the liquid solvent. The product liquid is separated from the solids and fed to purification. The residual solids are sent to the Liquefaction stage 2 reactor. Additional biomass is solubilized in stage 2. The product liquid is separated from the solids and fed to purification. The remaining biomass is fed into the Liquefaction stage 3 reactor. The 3rd stage solubilizes more biomass and solubilized products are concurrently reacted by catalyst with hydrogen. The residual biomass is then removed from the reactor, washed to recover entrained products, and then fed into a combustor/boiler/turbogenerator that provides heat for the process as well as electricity.

### *Purification/Concentration*

Liquid phase products from Liquefaction are fed forward to a purification step where inorganic ash components are removed via ion exchange. The purified stream is then fed to a triple effect vacuum evaporator and concentrated before catalytic upgrading. The evaporated water is sent to waste water treatment. The final product from this step is a concentrated purified hydrolysate.

### *BioForming Conversion Process and Product Separation/Recovery*

The purified hydrolysate enters the HDO reactor, containing a fixed catalyst bed in the presence of hydrogen gas. The sugars are converted into a mixture of alcohols, ketones, cyclic ethers, alkanes, acids, water, and other oxygenated compounds. The aqueous phase of the product is recycled back to the reactor inlet, while the organic liquid and gas phases are sent forward to the

DHOG reactor. The DHOG reactor contains a fixed catalyst bed and produces a mixture of alkanes, alkenes, and mono-oxygenates with a targeted carbon range of C8-C24.

The DHOG reactor product is separated in a flash separation vessel, with a light gas organic phase recycled back to the reactor inlet, the aqueous phase sent to WWT, and the organic liquid phase fed forward to the hydrofinishing reactor. In this final reaction, the organic liquid reacts over a fixed catalyst bed in the presence of hydrogen gas to remove any remaining oxygen in the product and saturate alkenes to alkanes. The product from the hydrofinishing reactor is then sent to product fractionation, where the hydrocarbon product is distilled into gasoline, jet, and diesel products.

***Wastewater Treatment:***

A wastewater stream is produced in this design that must be treated before it is safe to discharge back to the environment. The wastewater stream is processed via anaerobic digestion and aerobic digestion to digest organic matter in the stream. Aerobic digestion produces a cleaned water stream that will be safe to discharge to the environment and a sludge that is primarily composed of cell mass. This sludge is also burned in the boiler/combustor system.

***Combustor/Boiler/Turbogenerator:***

The combustor, boiler, and turbogenerator process section utilizes the various by-product and process waste streams to produce steam and electricity. The combustion of the recovered lignin, WWT sludge, WWT biogas, and process fuel gas produce enough steam and electricity to ensure the process is energy self-sufficient. Excess energy is available, above the plant needs, and is used to produce electricity for export to the grid.

***Utilities and Storage:***

All process water, cooling water, and electricity requirements throughout the process are modeled and tracked in the utilities section. Steam requirements and balances are accounted for in the combustor/boiler system. Cooling water used throughout the process is designed for a 28°C supply temperature.

## Total Capital Investment

The techno-economic analysis (TEA) includes the three steps described above (HTL, hydrolysate purification, BioForming) required to convert raw biomass (loblolly pine) into liquid fuels. The BioForming portion of the TEA includes the necessary purification required to introduce crude hydrolysate into the BioForming platform, conversion of hydrolysate to liquid fuels via the BioForming Platform, and final separations necessary to produce liquid fuel blendstocks (gasoline, jet, and diesel). Purification capital cost estimates are based on in-house values from Virent vendor quotes and equipment design. Scaled cost estimates were made from previous BioForming process estimates derived from the methods of Peters & Timmerhaus (P&T) (12). Metrics from P&T were then used to estimate direct equipment, installation, and indirect costs. The total capital investment (2007$) was determined by summing the purchased equipment costs, and multiplying by factors for direct and indirect expenses. All costs and assumptions of the combustor/boiler/turbogenerator section are consistent with the 2011 Humbird et al. design case [2].

## Variable Operating Costs

Variable operating costs were determined based on required raw materials, catalysts, waste handling charges, and by-product credits incurred during the operation of the process.

### *Biomass*

Feedstock costs are based on 2014 MYPP costs (as per the available information of the original FOA) for 2012 targets ($52/dry ton).

### *Catalyst Costs*

The cost of the catalysts used in the BioForming process were calculated on an annual basis.

### *Waste Treatment*

The operating costs associated with wastewater treatment was estimated at $0.53/MT WW, consistent with previous design reports.

### *Hydrogen*

The hydrogen feedstock was assumed to be $1.5/kg $H_2$ in 2014$ (cost provided by NREL). Hydrogen requirements were scaled from previous estimates on similar processes and incorporated into the TEA.

### *Labor and Maintenance*

Labor and maintenance costs have also been included in operating cost estimate under the general category of fixed costs. Total fixed cost charges were estimated at 9% of the TIC annually.

### *Co-Product Credits*

A co-product credit ($0.06/kWh) was taken for excess electricity produced from the turbogenerator from the burning of residual lignin and other by-product streams.

### *Annualized Operating Costs*

The feedstock cost used in this study was $52/dry ton. The operating costs for the catalyst makeup and disposal are included in the variable operating cost calculation. The co-product credit is based on the excess amount of electricity generated from the burning of lignin and other by-product streams.

### Return on Capital

A nominal 10% weighted average cost of capital.

### Production Cost

The cash cost of production includes all costs required to operate the facility including, biomass, catalysts, waste disposal and treatment, hydrogen, utilities and labor and maintenance. The profited cost is the cash cost of production plus the return on capital. A breakdown of the cost of production is shown below in Figure 20.

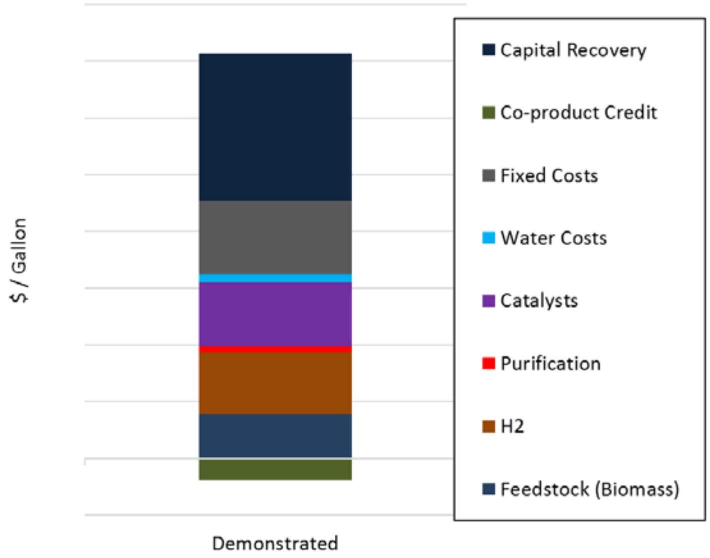

**Figure 20: Profited cost of production for demonstrated process configuration**

### Greenhouse Gas Analysis

The life cycle analysis (LCA) of the Virent multistage hydrothermal liquefaction process utilized the 2015 GREET.NET (ANL, 2015) platform. GREET.NET uses the net process inputs and outputs from the integrated heat and material balance. The process inputs included poplar, hydrogen, catalysts and electricity displacement based on the U.S. electrical mix. The initial calculations indicated a potential reduction of >70% reduction versus the 2005 petroleum baseline. The largest sensitivities for the LCA were H2 consumption and electricity export from the facility.

## Project Management

### Project Planning

At the outset of the project, a comprehensive Project Management Plan was assembled and a Project Work Plan created. There was frequent reporting to DOE on the project and technical performance. The Virent project team hosted monthly calls and prepared quarterly reports which were shared amongst the Virent and DOE team members. Quarterly technical and financial reports were filed with the DOE project team as prescribed in the contract documents and Virent provided DOE with project highlights suitable for public dissemination.

### Reporting & Control

Reports and deliverables were provided in accordance with the Federal Assistance Reporting Checklist following the instructions included therein.

Throughout the project a project management team was responsible for reporting and controlling the project. This consisted of the following monthly and quarterly tasks:

- Quarterly reporting. Reporting consisted of a PMP, narrative, and SF-425. These reports were completed quarterly and on-time throughout the project.

- Milestone reports. The milestone reports were submitted throughout the project to provide background information regarding each individual milestone as the Nighthawk project team achieved them and to serve as a deliverable marking the completion of the milestone.
- Budget Control. The Nighthawk project management team adhered to the budget and communicated with the DOE project team to seek guidance and approval whenever changes were required to meet the project milestones.
- The Nighthawk project team met monthly via teleconference throughout the project to discuss the current state of the project, share progress, and discuss future work.

### Peer Review

During the project period two Project Peer Review meetings were hosted by the Bioenergy Technologies Office (BETO) in 2015 and 2017. Both meetings were attended by Virent personnel and the Nighthawk project was reviewed by the DOE, members of the public, industry advisors, and members of the academic community. Virent presented upon the current state of the project, took questions, and responded to questions posed by the reviewers.

### CAAFI Webinar

### Final Reporting

Final reporting will conclude with the submission of this report and the required forms outlined in the Federal Assistance Reporting Checklist. The final reporting documentation will consist of:

- This final technical report.
- Patent certification (DOE 2050.11)
- SF-425 covering the entire span of the project.
- Final property report (SF-428 & SF-428B).

## References

1. Toor S, Rosendahl L, Rudolf A. (2011) Hydrothermal liquefaction of biomass: A review of subcritical water technologies. Energy. 2328-2342
2. Humbird D, Davis R, Tao L, C K, Hsu D, Aden A, …, Dudgeon D. (2011) Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol - Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover. Golden: NREL – DOE.