Fractional Multistage Hydrothermal Liquefaction of Biomass and Catalytic Conversion into Hydrocarbons

8 March, 2017

Technology Area Review: Thermochemical Conversion

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WBS: 2.5.5.401

VIRENT

Goal Statement

Project Goal – Develop a novel Multistage Hydrothermal Liquefaction (HTL) of biomass and integrate with Virent's Catalytic BioForming® Process to efficiently produce cost effective "drop-in" fuels from woody biomass and corn stover, with particular focus in maximizing jet fuel and diesel yields.

- **Developing commercially Viable Bioenergy Technology**
  - **Improve pretreatment strategies**
  - **Improve fuel yields**
- **Reduction of Greenhouse Gas Emission**
  - **Non-Food Feedstock** – Woody Biomass, Corn Stover
  - **Improve fuel yields**
- **Process Generates "Direct Replacement" Hydrocarbons compatible with today's transportation infrastructure**
  - **Distillate Range Products** for use as either jet fuel or diesel fuel
  - **"Advantaged" Jet and Diesel Fuels**
- **Relevance and Tangible Outcomes for the United States**
  - **Promotes National Security**
  - **Growing a Sustainable future**
  - **Generating green jobs**

Quad Chart Overview

Timeline

- Project Start: October 2013
- Project End: March 2017
- Percent complete: ~95%

Budget

	FY14 Costs	FY15 Costs	FY16 Costs	FY17-End Costs Est.
DOE Funded	$666,358	$1,736,902	$623,368	$105,000
Virent Cost Share	$192,538	$540,778	$508,818	$15,000

Barriers

- Tt-B: Feeding Wet Biomass
- Tt-D: Biomass Pretreatment
- Tt-F: Deconstruction of Biomass to Form Bio-Oil Intermediates
- Tt-J: Catalytic Upgrading of Bio-Oil Intermediates to Fuels and Chemicals

Partners

- Idaho National Laboratory
  - Feedstock Supply
  - Biomass Pretreatment

1 - Project Overview

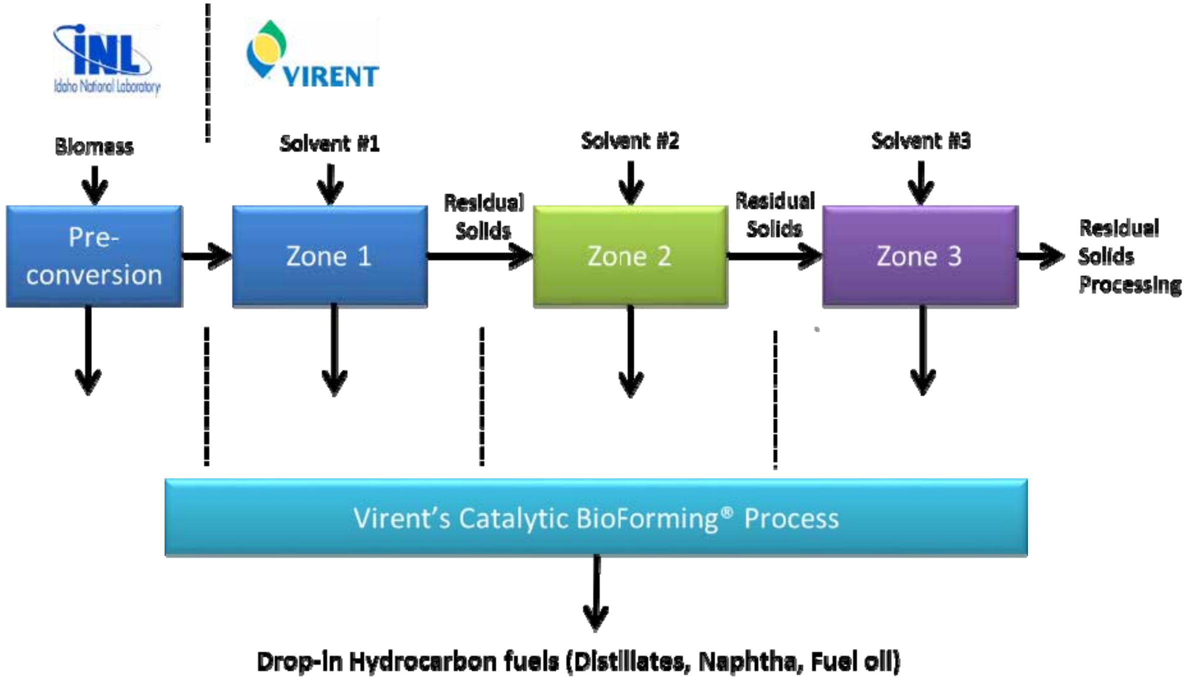
- Convert lignocellulosic feedstocks to drop-in liquid fuels
- Multistage Hydrothermal Liquefaction
  - Develop multistage HTL utilizing appropriate solvents and process conditions to convert woody biomass and corn stover to liquid intermediates that can be catalytically upgraded to “direct replacement” hydrocarbons
  - Progress from Applied Research to Preliminary Investigation
  - Focus on integration with Virent BioForming platform
- Pilot Build
  - Design, build, and operate a continuous pilot for multistage HTL technology
- Catalytic Upgrading
  - Integrate HTL technology with Virent BioForming catalytic upgrading to produce “direct-replacement” hydrocarbon liquid fuels
  - Focus on distillate fuels – jet fuel and diesel
- TEA and LCA
  - Complete Techno-Economic Analysis and Life Cycle Analysis

2 – Approach (Management)

- *Project Management approach*
  - *Gantt Chart for 3 year project*
    - *Weekly team meetings*
    - *Monthly project updates with DOE*
    - *Quarterly reporting*
  - *Key Milestones*
    - *TRL-2 Milestones (September 2014)*
    - *TRL-3 Milestones (March 2016)*
    - *Stage Gate Review (March 2016)*
    - *Project End (March 2017)*
- *Critical Market and Business Success factors*
  - *Establish Cost and Technical Targets for Catalytic derived hydrocarbon fuels based on TEA*
  - *Market Size and Opportunity*
- *Potential Market and Business Challenges*
  - *Crude Oil Prices, Financing of Plant, Government Policy, Biomass Cost*

2 – Approach (Technical)

- Overall Technical Approach



- Each zone targeted solubilizing a specific biomass fraction (hemicellulose, cellulose, or lignin) with an appropriate solvent
- Solvents may be internally generated or economically obtained

- Critical Success Factors – Feedstock, Biomass Pretreatment, Deconstruction, Hydrolysate Conditioning, Catalytic Conversion, Product Certification, Overall Process Economics
- Potential Challenges – Biomass to usable carbon, HTL product integration into catalytic upgrading, Intensify process by eliminating processing steps

2 – Approach (Technical)

- **Critical Success Factors**
  - **Ash Removal**
    - Necessary to Reduce Potential Catalyst Poisons
  - **Carbon Recovery**
    - Maximize carbon recovery from hemicellulose and cellulose
    - Maximize the liquefaction and conversion of lignin components
    - Maximize carbon conversion in the catalytic conversion to desired liquid hydrocarbon
  - **Process Economics** – Reduction in capital and operating cost of biomass to jet fuel distillate

- **Potential Challenges**
  - **Removal** of ash components in preconversion and processing steps.
  - **Improve yields** of “convertible carbon” intermediate streams through HTL process optimization
  - **Process Intensification** through the potential elimination of HTL and/or catalytic processing steps

2 – Approach (Technical)

INL Tasks

- Supply formatted loblolly pine to Virent upon request (up to three shipments)
  - Characterize with proximate/ultimate, ash composition and calorific analyses
- Perform chemical preconversions on corn stover using the Chemical Preconversion System and subsequent bench top extractions/washes
  - Characterize ash and nitrogen removal and changes to ash composition
    - SiO_2, alkali metals, alkaline earth metals and nitrogen
  - Supply samples to Virent for testing
- Optimize chemical preconversion process using sequential alkali/acid treatments and extractions/washes based on Virent's input for desired results

3 – Technical Accomplishments / Progress / Results

Milestone	Milestone Title	Description
A.1.ML.1	Stover Preconversion Performance Target	Demonstrate total ash content <1% with >90% carbon conservation
A.2.ML.1	TRL-2 Liquefaction Performance Target	Demonstrate carbon efficiency of >60% for HTL from biomass to soluble carbon in batch tube experiments
A.3.ML.1	TRL-2 Catalytic Upgrading Performance Target	Demonstrate >65% yield to liquid fuel products with model feeds
B.2.ML.1	TRL-3 Liquefaction Performance Target	Demonstrate carbon efficiency of >70% for HTL from biomass to soluble carbon
B.3.ML.1	TRL-3 Catalytic Upgrading Performance Target	Demonstrate >50% yield to liquid fuel products from biomass, with 70% recovery in catalytic step
B.4.ML.1	TRL-3 TEA and LCA	Complete intermediate TEA and LCA on the process configuration. Demonstrate >60% GHG reduction

3-Technical Results

Stover Pre-conversion

Enhanced ash reduction with loss of organic carbon.

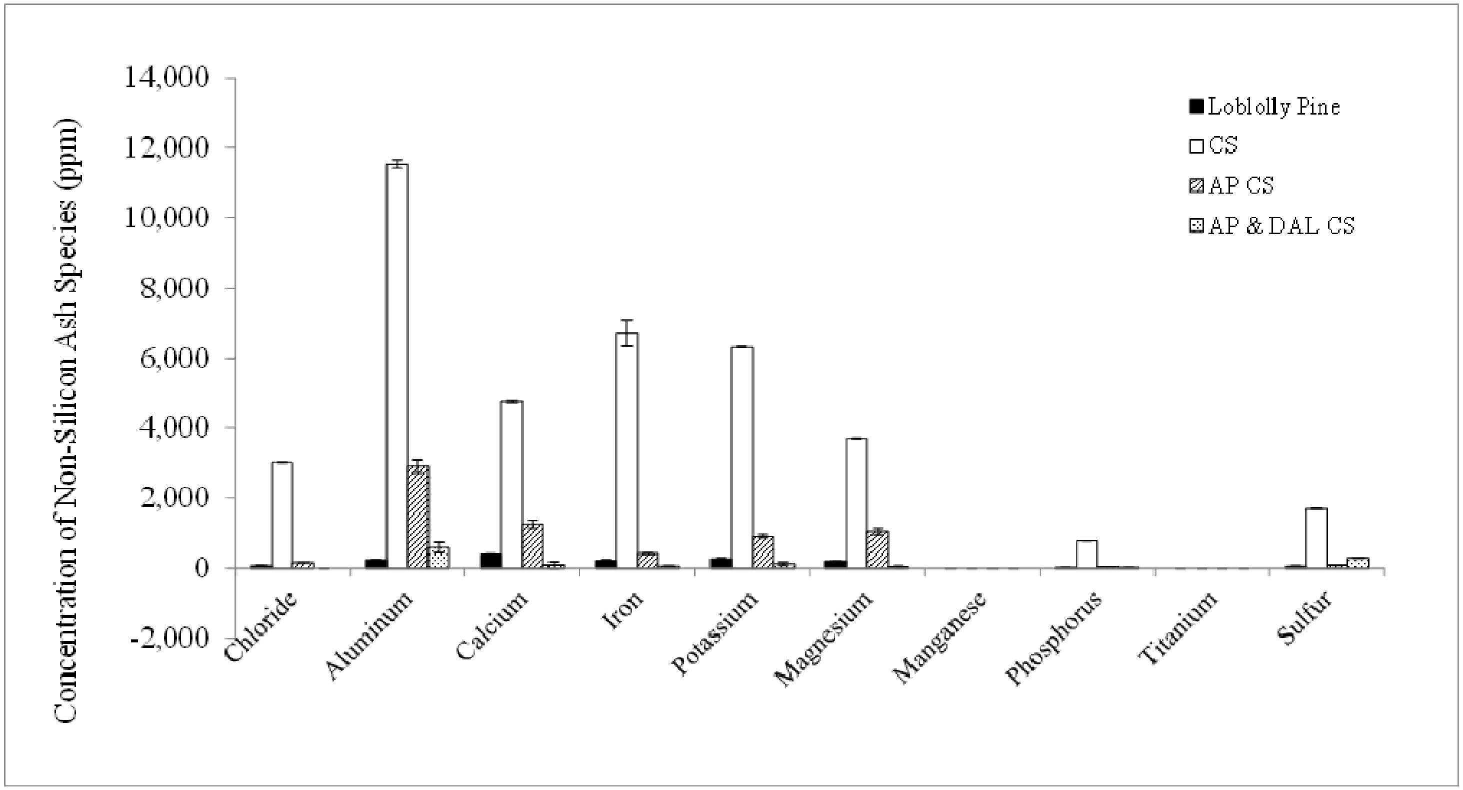
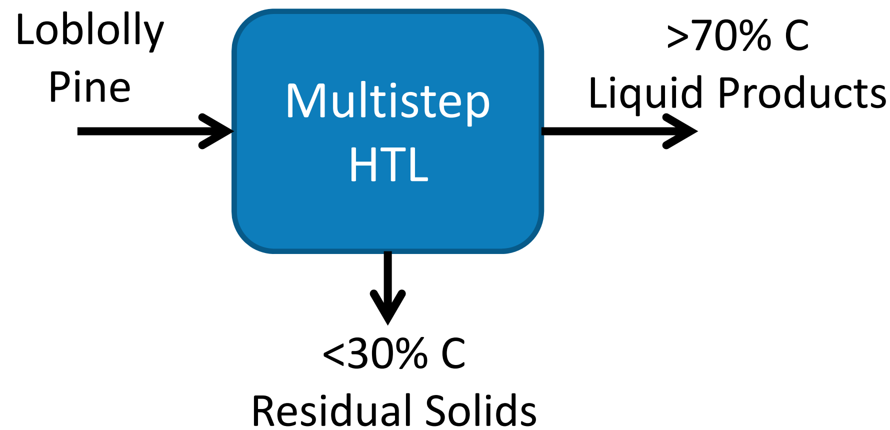
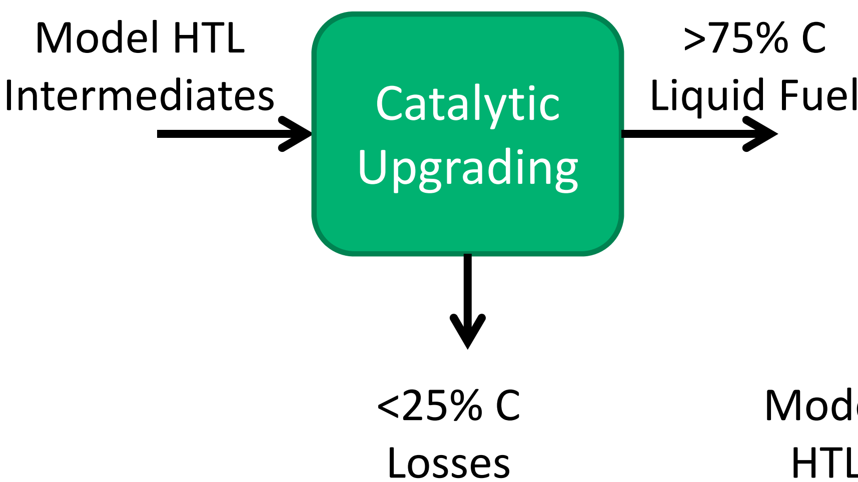


Figure: Comparison of non-silicon ash species content in loblolly pine (LP), multi-pass corn stover (CS), alkaline preprocessed and extracted corn stover (AP CS) and alkaline preprocessed, extracted and dilute acid leached corn stover (AP & DAL CS).

3 – Technical Results – TRL-2 Yield Milestones

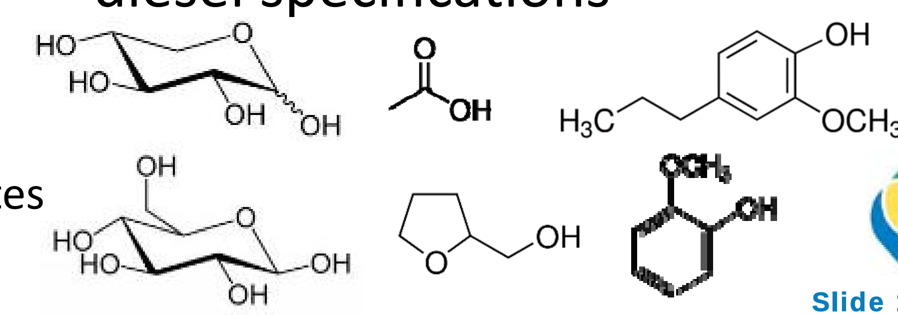
- Milestone of >60% C to liquid products from real feedstock demonstrated (>70% achieved)
- Hemicellulose, cellulose, and lignin liquefied





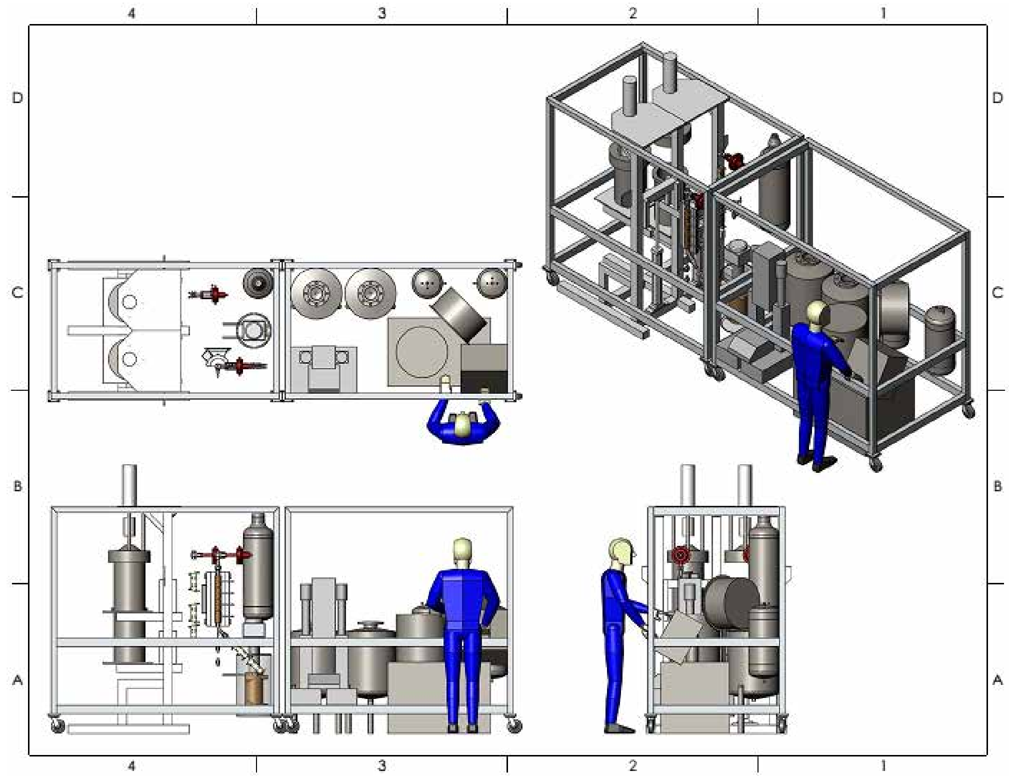
- Milestone of >65% C to liquid fuels from model HTL intermediates demonstrated (>75% achieved)
- Finished fuel meets jet fuel and diesel specifications

Model HTL Intermediates



3 – Technical Results – Pilot Build

- Initial design of continuous HTL pilot completed
    - Feed System, HTL Reactor, Solid/Liquid Separation, Product Collection
- All major equipment identified, utilizing scalable and economical process design
- Safety: HAZOP and Pre-Safety Start-up
- Build completed mid-2015



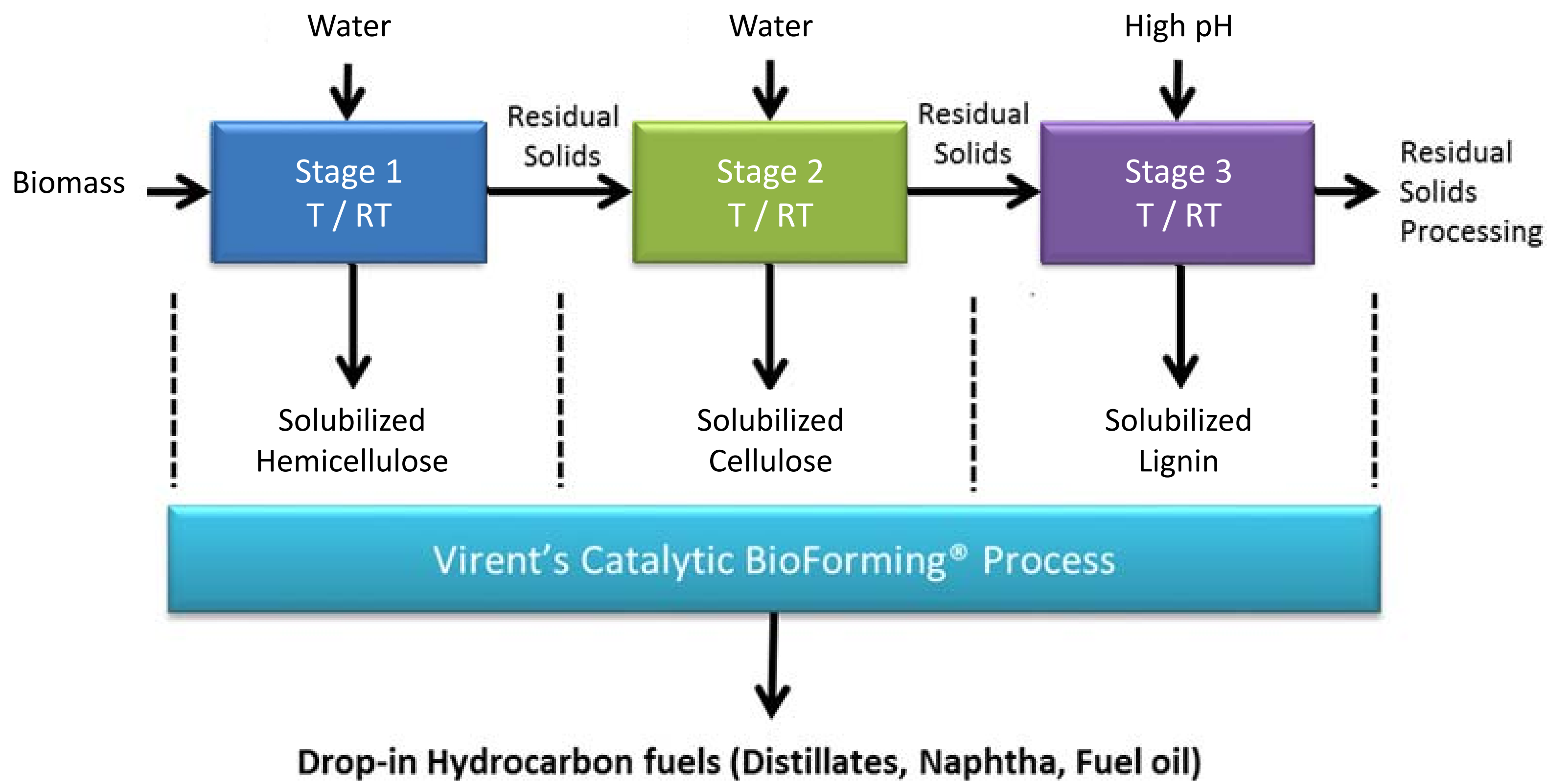
3-Technical Results – Pilot Build

HTL Reactor

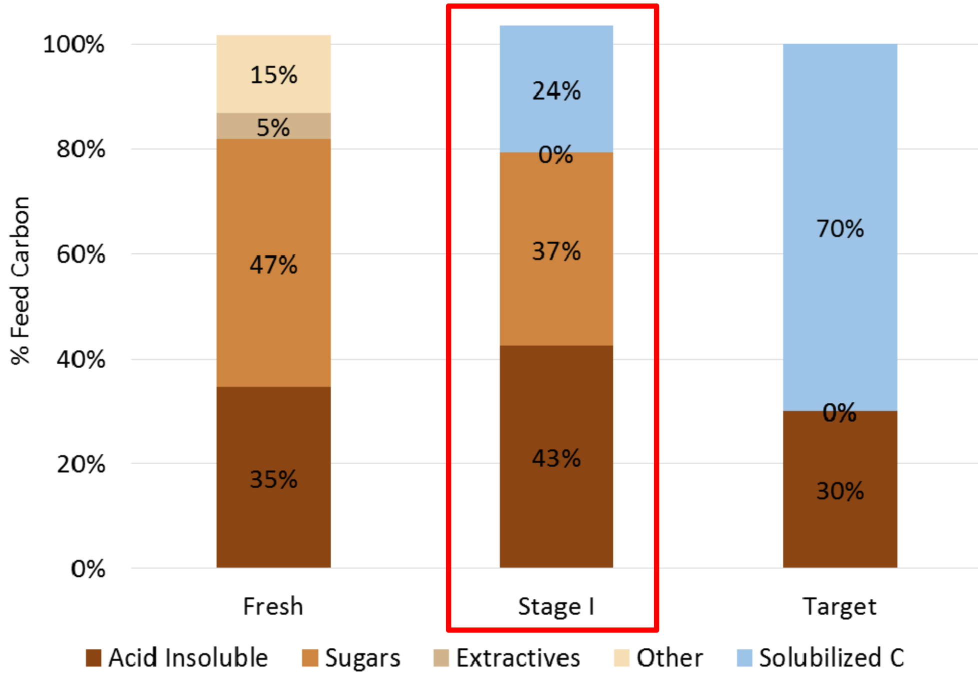
Slurry Feed system

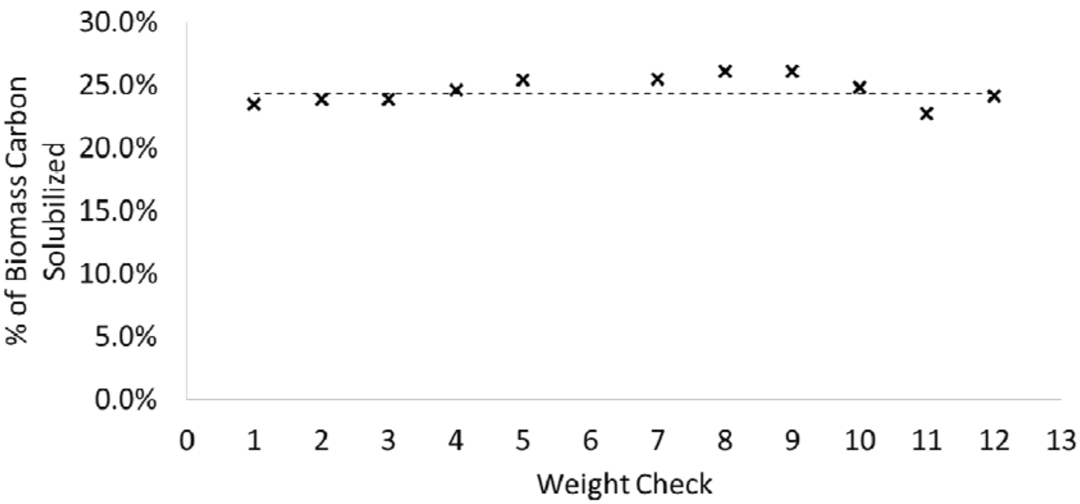
Collection and Separation

3-Technical Results –
TRL 3 - Proof of Concept



HTL 1 – Extractives + Hemicellulose

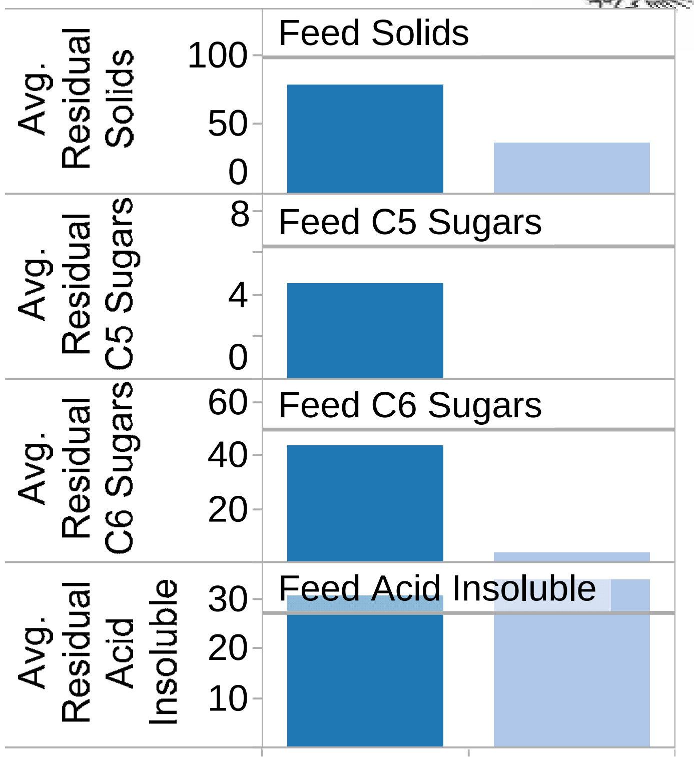




- Other and Extractives completely solubilized
- Sugars disappearance
  - Hemicellulose solubilization (C5 sugars)
  - Increase in Acid Insoluble – evidence of undesirable recombination
- Production run
  - Over 13 days of operation
  - 13 kg of residual solids generated
  - 10 liters of concentrated liquid hydrolysate generated

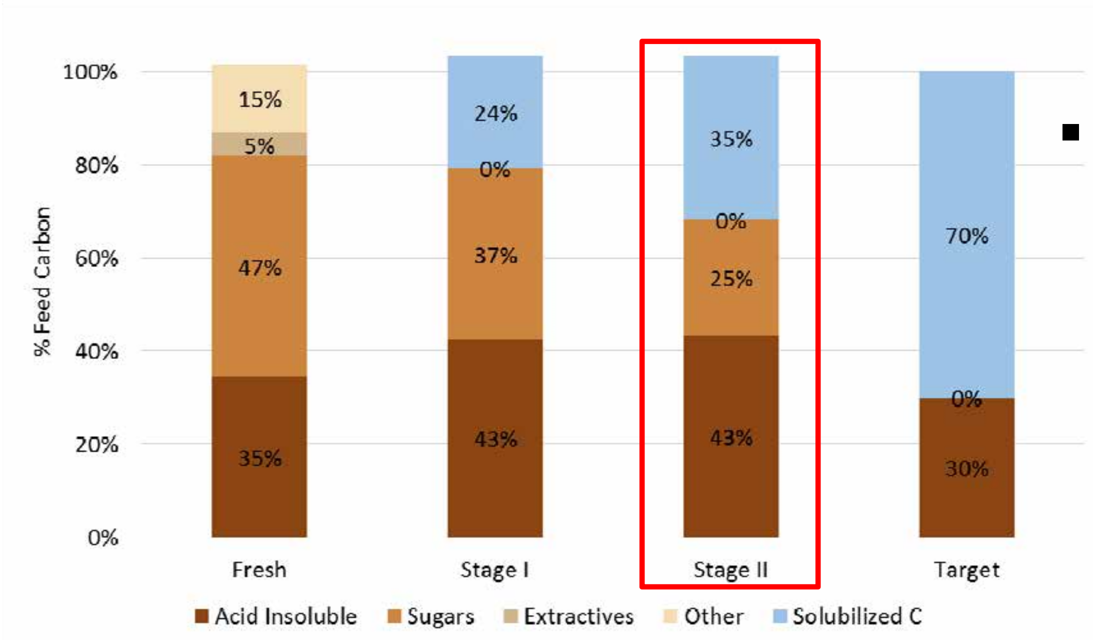
HTL 2 – Cellulose Scoping

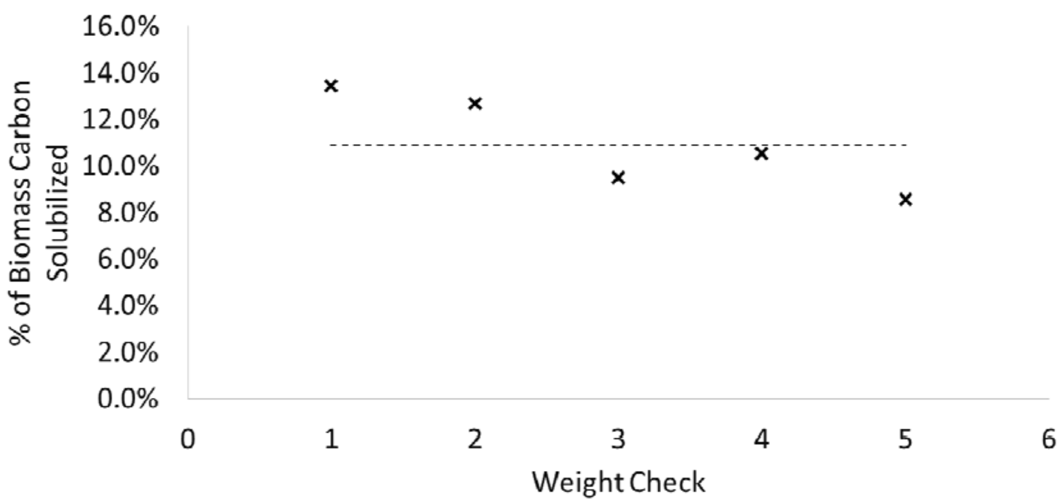
- Crystalline cellulose requires higher temperatures and/or longer residence times to break glycosidic bonds
- TRL-2 solvent scoping suggested water could solubilize most of the cellulose in fresh biomass
- Temperature vs. Residence Time



Fresh Biomass   Stage 1 Residual Solids

HTL 2 – Cellulose

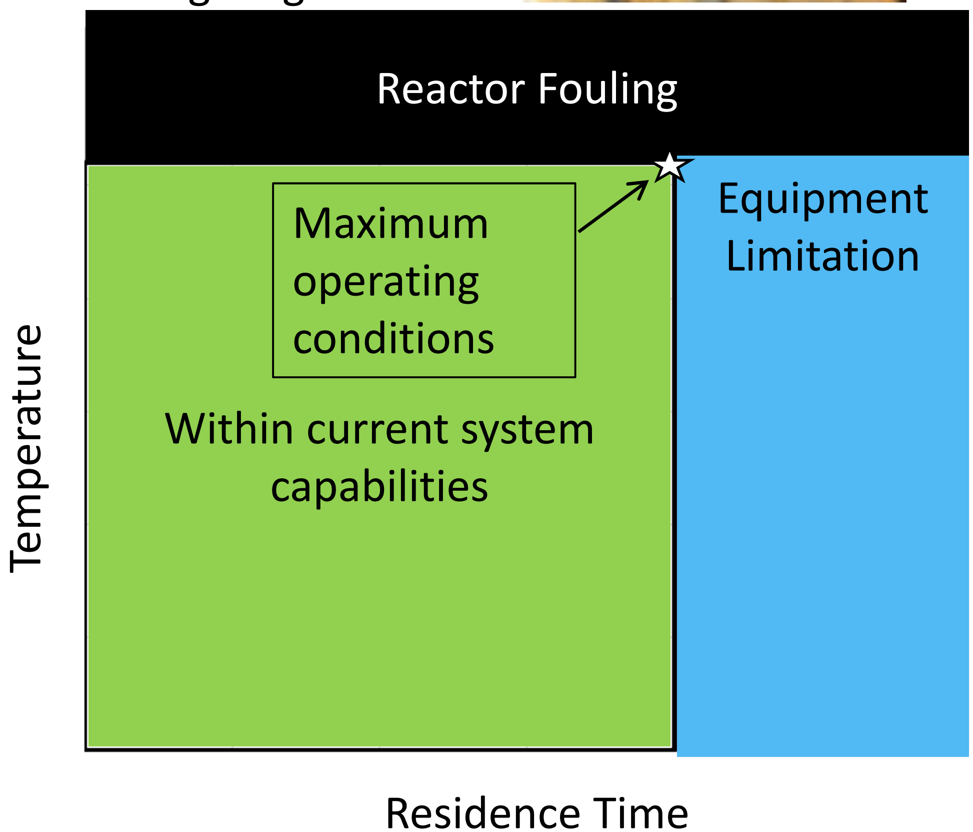




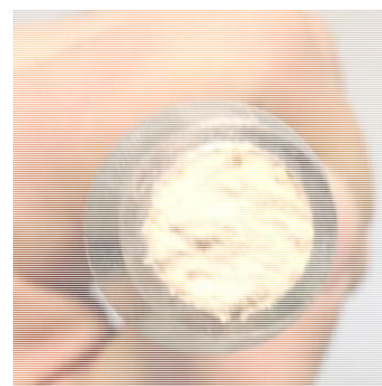
- Sugars disappearance
  - Remaining Hemicellulose (C5) and moderate Cellulose (C6) solubilization
  - No change in Acid Insoluble – no evidence of undesirable recombination
- Production run
  - Over 5 days of operation
  - 4 kg of residual solids generated
  - 2 liters of concentrated liquid hydrolysate generated

HTL 2 – Cellulose Scoping

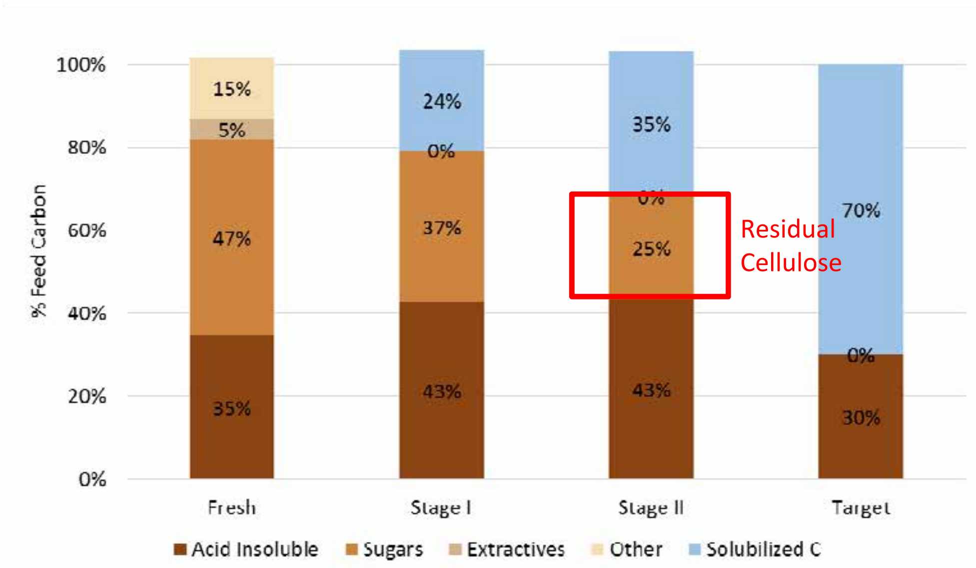
Repeated thermal degradation experienced at higher temperature using Stage 1 solids



Operational issues due to biomass settling and plugging at longer residence times

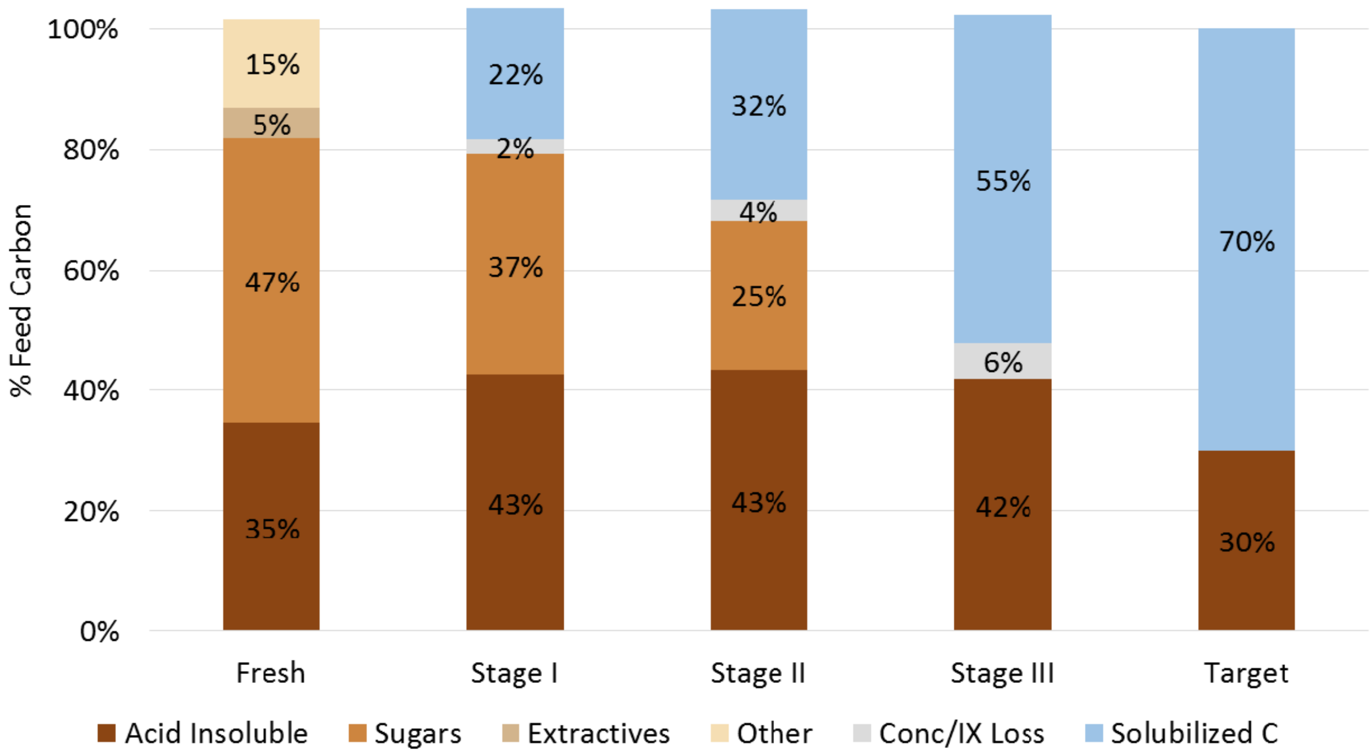


HTL 3



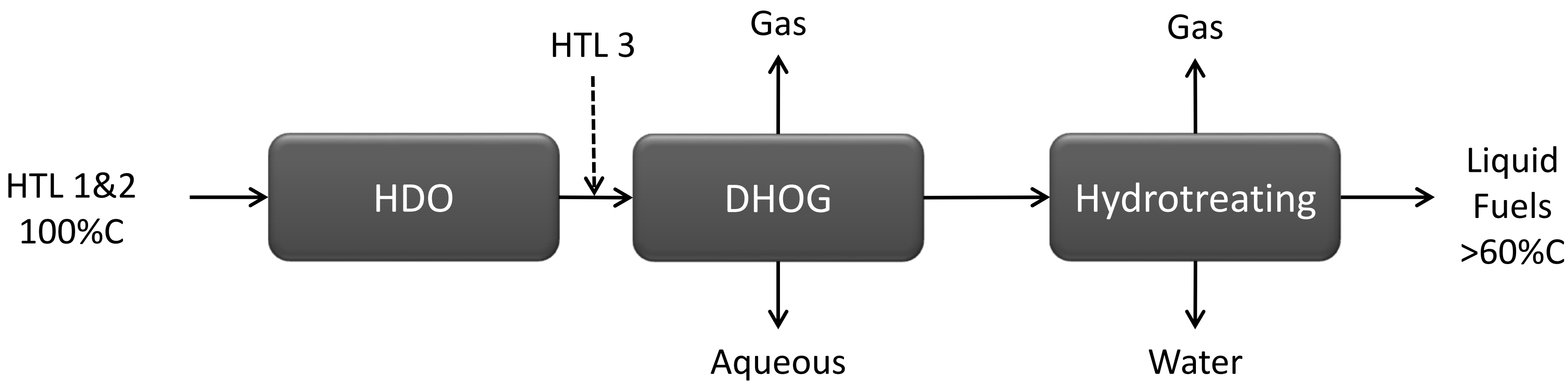
- Residual cellulose
  - Complete cellulose removal desired prior to lignin removal
  - Lignin removal requires higher temperatures that result in higher losses due to light ends formation.
- Stage 3
  - Focus on remaining cellulose prior to lignin solubilization

Final HTL Yields – TRL-3



55% of feed carbon solubilized to liquid phase through HTL 1-3 + Concentration/IX

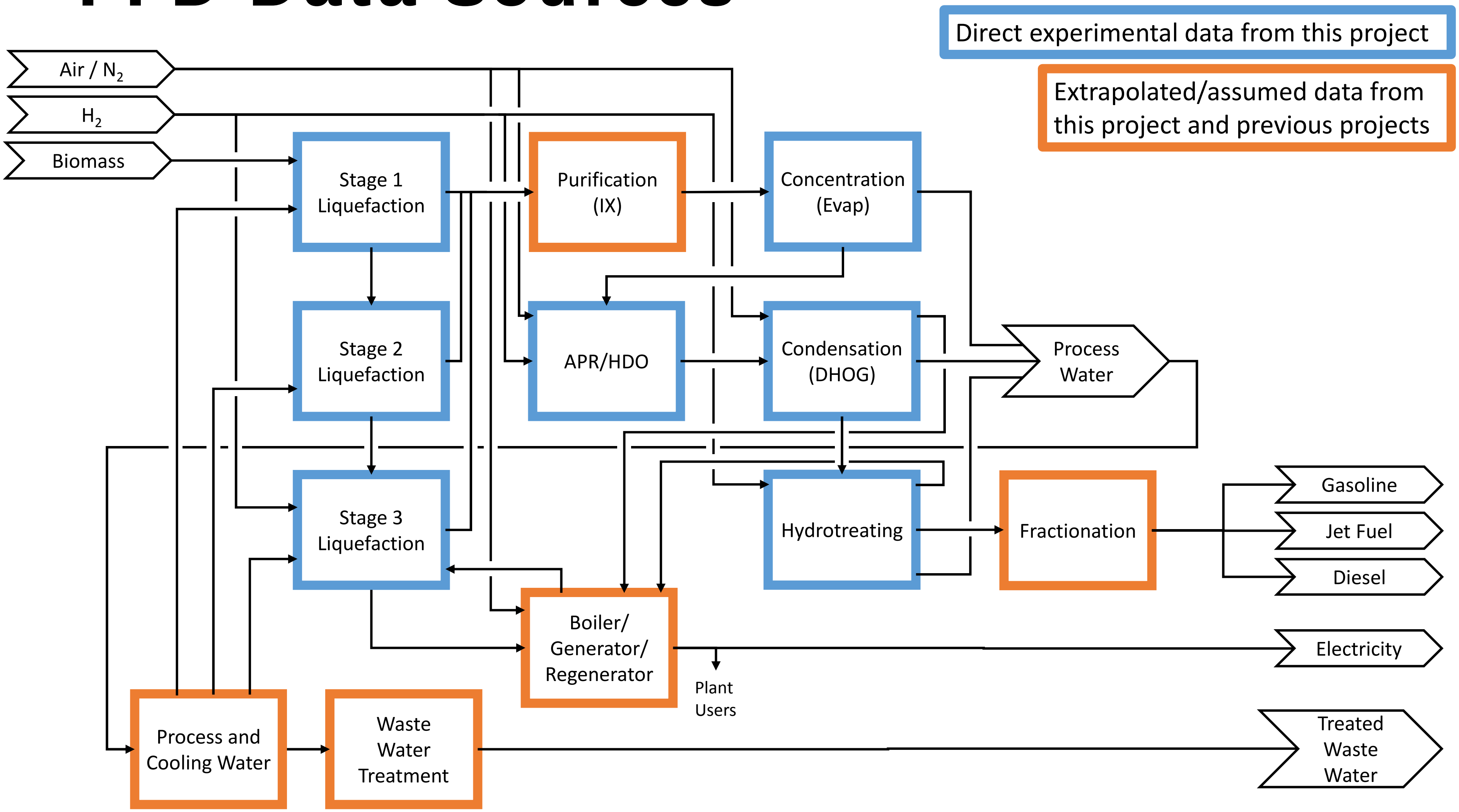
Demonstrated Performance



- Similar run plan to previous Project Validations
- Performance averaged over 4 days and 7 weight checks
- 24/7 coverage to ensure good Operations
- System startup with corn syrup to maximize steady-state time with biomass hydrolysate

3-Technical Results – TEA & LCA

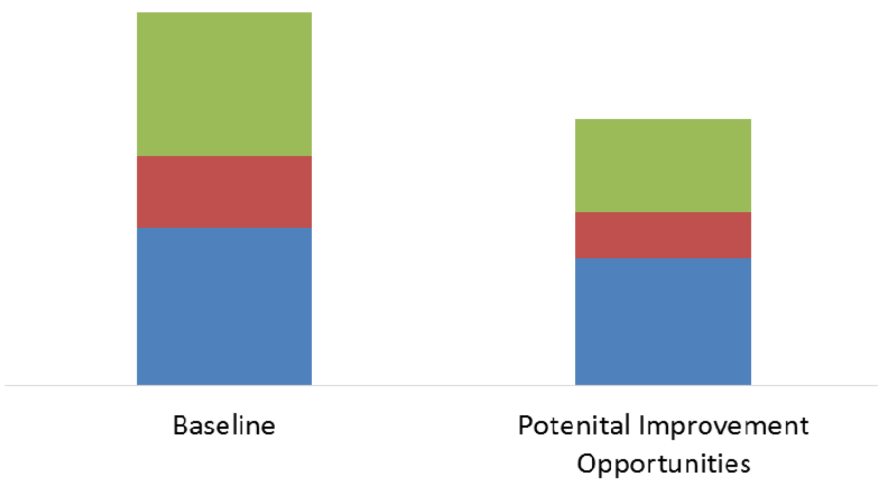
PFD Data Sources



3-Technical Results – TEA & LCA

TEA

- 2000 Metric Tons/Day loblolly pine
- Integrated laboratory data
- Aspen process model & factored estimates
- Sensitivities
  - Overall Process Yield
  - Capex



LCA:

- Utilized HMB from economics as baseline information
- Utilized Greet.net 2015 for datasets
- LCA results ranged from a reduction of 72 to 47% versus the 2005 petroleum baseline
- Largest sensitivities to LCA
  - Electricity Export
  - H2 Consumption

Project Milestones

Budget Period 1

Milestone	Milestone Title	Description	Performance Virent Estimate
A.1.ML.1	Stover Preconversion Performance Target	Demonstrate total ash content <1% with >90% carbon conservation	
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4 – Relevance

- *Contributions to meeting the platform goals and objectives of the BETO Multi-Year Program Plan*
  - If successful, project would address the strategic goal to develop commercially viable technologies for converting biomass into energy-dense, fungible finished liquid fuels, such as renewable jet and diesel.
  - This project utilizes analysis interface through the use of TEA and LCA to inform feed collection methods and processing steps.
  - Working with INL will investigate feedstock supply, preconversion technologies, and logistics interfaces.
  - Biofuels distribution infrastructure interface will be addressed through ASTM certification of resulting jet fuel, and diesel product qualification.
  - Addresses barriers such as
    - Tt-B Feeding Wet Biomass
    - Tt-C Biomass Pretreatment
    - Tt-F Deconstruction of Biomass to Form Bio-Oil Intermediates
    - Tt-J Catalytic Upgrading of Bio-Oil Intermediates to Fuels and Chemicals
    - Tt-K Product Finishing
    - Tt-L Knowledge Gaps in Chemical Processes

- *Applications of the expected outputs in the emerging bioenergy industry*
  - Results from this project provide technical viability of combining a biochemical conversion technology frontend with a chemical (catalytic) conversion technology to generate “direct replacement” hydrocarbons from a lignocellulosic feedstock.
  - Project has resulted in 1 US Patent application

5 – Future Work

- Virent/DOE Mutual Termination of Project
  - Early TRL Technology
  - Virent near term Commercial Focus
  - Change in Key Personal
- Final Reporting and Project Close-out

Summary

1. Overview
   - Converted lignocellulosic feedstocks to drop-in liquid fuels
   - Developed novel Multistage Liquefaction and integrate with Virent's BioForming Catalytic Upgrading
2. Approach
   - Progressed from TRL-2 Applied Research to TRL-3 Proof of Concept
3. Technical Results
   - TRL-2 Applied Research completed: yield milestones met, initial kinetic model developed, pilot design completed
   - TRL-3 Proof of Concept progressed towards TRL-4
4. Relevance
   - Demonstrate technical and economic viability of process
5. Future Work
   - Project Close-out

Additional Slides

Peer Evaluation

Responses to Previous Reviewers' Comments

- Comment: Hydrogen consumption needs to be quantified and addressed. *Hydrogen consumption is quantified and the consequences are addressed in the TEA and LCA*

- Comment: TEA analysis needs to be carried out before or in parallel with experiments. *TEA was carried out in parallel with experiments and further detailed with more complete data.*

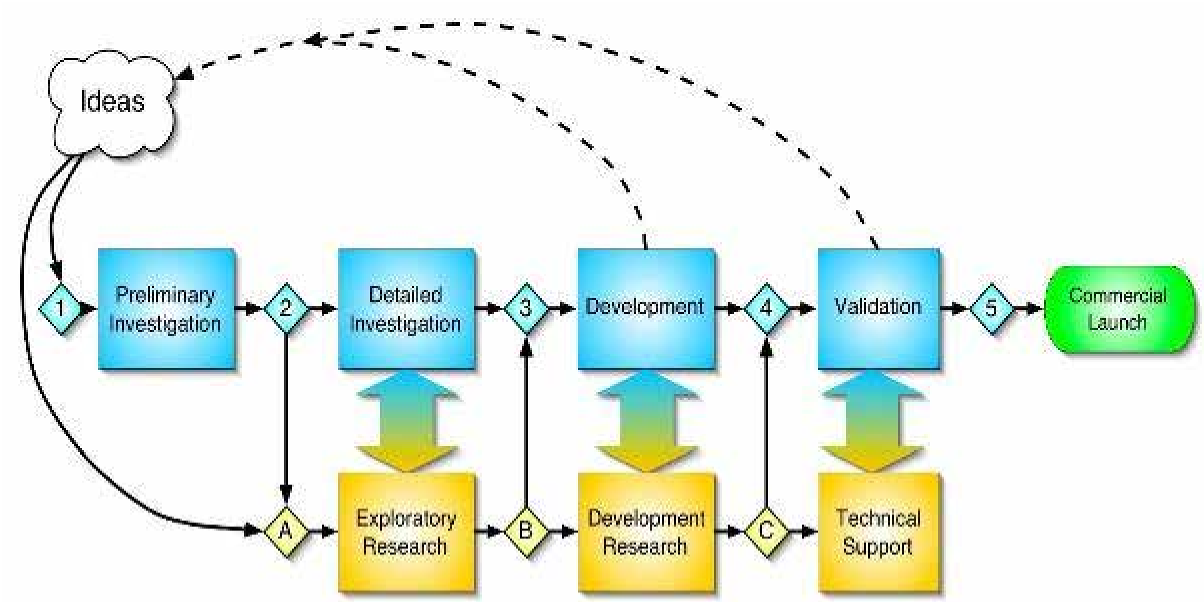
- Comment: Unrealistic expectation of contaminant removal. *The project baseline was completed with a low-ash loblolly pine. Details of contaminant removal from corn stover will allow for an economical comparison of differing feedstocks.*

Go-No Go Review

- Go-No Go Review held in March 2016
- Review focused on six main project milestones from Budget period one.
  - Successfully achieved three milestones and made significant progress towards achieving the other three
  - Proposed equipment modification to meet TRL-3 milestones
  - Proposed two potential paths forward
- DOE approved to move forward with completion of TRL-3 activities
- Additional stage-gate added prior to moving forward to TRL-4
- Contracting updated with updated budget and timeline

2. Approach (Technical)

Current State of Technologies



- Currently the Nighthawk project is mid Stage 2 which correlates to TRL-3.
- Completion of this project would put the project at the end of Stage 3 and ready to advance to TRL-5.