Fractional Multistage Hydrothermal Liquefaction of Biomass and Catalytic Conversion into Hydrocarbons

8 March, 2017
Technology Area Review: Thermochemical Conversion
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Presenter: Andrew Held
Virent, Inc
WBS: 2.5.5.401

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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**

<table>
<thead>
<tr>
<th></th>
<th>FY14 Costs</th>
<th>FY15 Costs</th>
<th>FY16 Costs</th>
<th>FY17-End Costs Est.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE Funded</td>
<td>$666,358</td>
<td>$1,736,902</td>
<td>$623,368</td>
<td>$105,000</td>
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<td>Virent Cost Share</td>
<td>$192,538</td>
<td>$540,778</td>
<td>$508,818</td>
<td>$15,000</td>
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**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

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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
    - SiO₂, 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

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<td>Complete intermediate TEA and LCA on the process configuration. Demonstrate &gt;60% GHG reduction</td>
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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
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-Techinal Results – TRL 3 - Proof of Concept

Virent’s Catalytic BioForming® Process

Drop-in Hydrocarbon fuels (Distillates, Naphtha, Fuel oil)
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
- **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
Repeated thermal degradation experienced at higher temperature using Stage 1 solids

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

- Reactor Fouling
  - Maximum operating conditions
    - Within current system capabilities
  - Equipment Limitation
- Temperature
- Residence Time
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
PFD Data Sources

- Direct experimental data from this project
- Extrapolated/assumed data from this project and previous projects

Stage 1 Liquefaction
- APR/HDO
- Condensation (DHOG)
- Purification (IX)
- Concentration (Evap)

Stage 2 Liquefaction
- APR/HDO
- Condensation (DHOG)

Stage 3 Liquefaction
- Hydrotreating

Boiler/Generator/Regenerator
- Waste Water Treatment
- Plant Users

Process and Cooling Water

Gasoline
Jet Fuel
Diesel
Electricity
Treated Waste Water
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

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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.