Catalytic Upgrading of Thermochemical Intermediates to Hydrocarbons: Conversion of Lignocellulosic Feedstocks to Aromatic Fuels and High Value Chemicals

25 March, 2015

Technology Area Review: Thermochemical Conversion

Randy Cortright PhD

Virent, Inc

WBS: 2.3.1.406

VIRENT

Goal Statement

Project Goal –Develop and demonstrate integration of Virent's lignocellulosic biomass Solvolysis technology with Virent's BioForming® process to generate aromatic-rich hydrocarbon products for use in either fuels or high value aromatic chemicals applications.

- **Biomass to Drop in Hydrocarbons**
  - Liquefaction of Biomass and Stabilization of the Intermediates using Virent proprietary catalysts and catalytically derived solvents.
  - Product Synthesis and Upgrading using catalytic condensation to produce aromatic rich hydrocarbon products that can be used as either fuels or high-valued aromatic chemicals
- **Developing a Commercially Viable Bioenergy Technology**
  - Demonstration of a thermochemical process to provide information relevant to scale-up and process integration.
- **Reduction in Greenhouse Gas Emissions**
  - Renewable feedstock – Forest harvest residuals, corn stover, sugarcane bagasse, etc.
  - Full utilization of biomass including lignin rather than a carbohydrate ONLY philosophy
  - Cradle to grave analysis shows a large reduction in the environmental impact increasing the overall sustainability.
- **Relevance and Tangible Outcomes for the United States**
  - Promotes national security through decreased dependence on foreign oil
  - Generates a sustainable future for petroleum derived products with renewable resources
  - Stimulates economic growth through generating jobs and a bioenergy industry

Quad Chart Overview

Timeline

- Project Start: October 2011
- Project End: September 2015
- Percent complete: ~85%

Barriers

- Tt-A: Feeding Dry Feedstock
- Tt-F: Deconstruction of Biomass to Form Bio-Oil Intermediates
- Tt-J: Catalytic Upgrading of Bio-Oil Intermediates to Fuels and Chemicals
- Tt-H: Intermediate Stabilization and Vapor Cleanup

Budget

	FY10 –FY12 Costs	FY13 Costs	FY14 Costs	FY15-End Costs
DOE Funded	$553,508	$1,038,015	$796,449	$1,612,028
Virent Cost Share	$452,870	$849,285	$651,640	$1,318,932

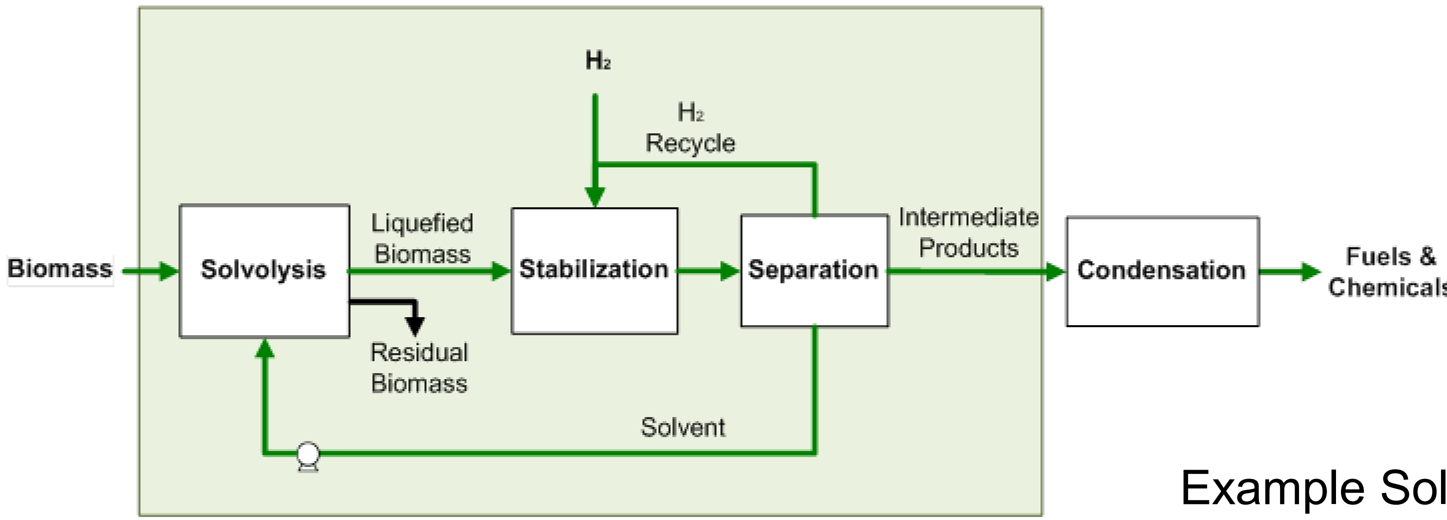
Partners

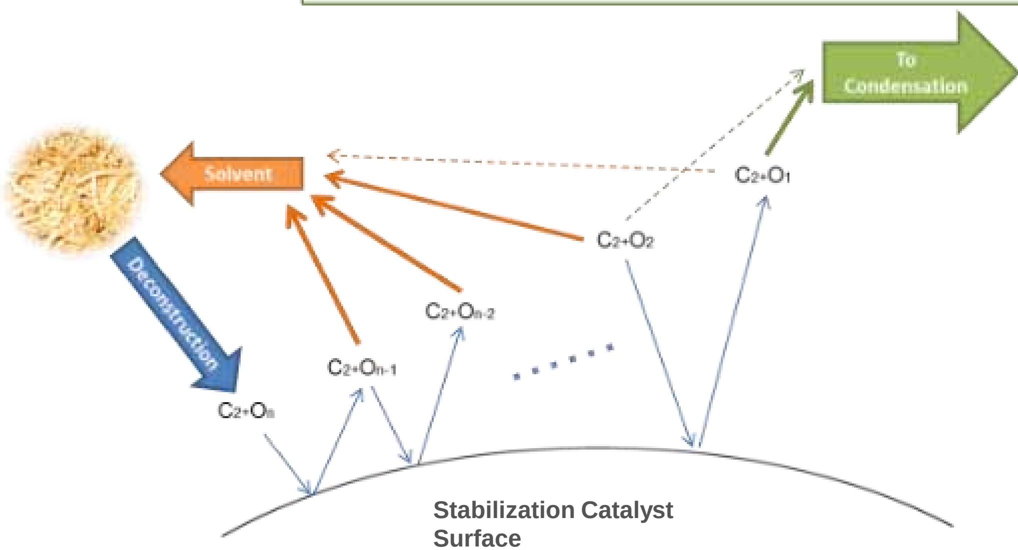
- Iowa State University
  - Feedstock Processing

1 - Project Overview

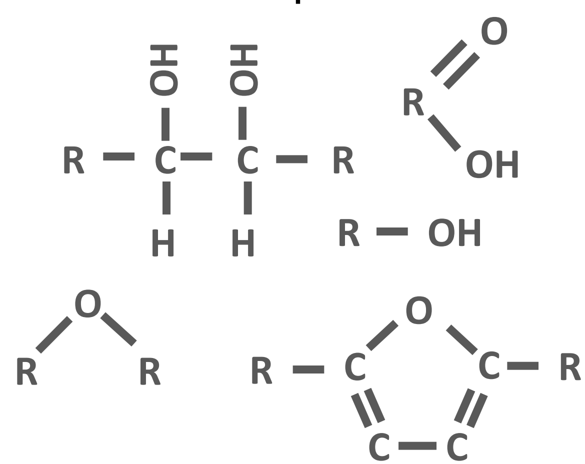
- **Project Goal** –Develop and demonstrate integration of Virent's lignocellulosic biomass Solvolysis technology with Virent's BioForming® process to generate aromatic-rich hydrocarbon products for use in either fuels or high value aromatic chemicals applications
  - **Demonstrate** with multiple feedstocks (Residual Wood, Corn Stover, Bagasse)
  - **Maximize** carbon yields from biomass to desired products (aromatic-rich reformate)
  - **Modifications** of Virent's Catalytic Oxygenates to Aromatic (COTA) Process to maximize the carbon yields and product quality in the final product.
  - **Collect** pilot plant data to confirm scale-up viability, economics, and LCA of integrated process.
  - **Demonstrate** operability of the fully integrated lab-scale biomass to aromatics process via a 2000 hr lifetime run.

2 – Approach (Technical)
Overall Technical Approach



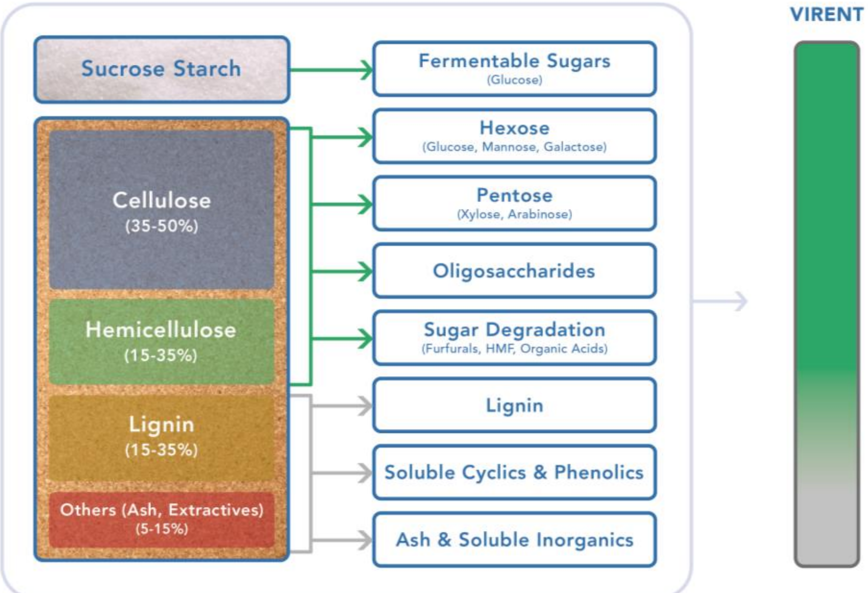


Example Solvent Compounds



-Qiao, Ming; Woods, Elizabeth; Myren, Paul; Cortright, Randy; and Connolly, Sean; Patent Application US 13/339720 Publication No. 20120318258 Solvolysis of Biomass to Produce Aqueous and Organic Products

2 – Approach (Technical)
Critical Success Factors

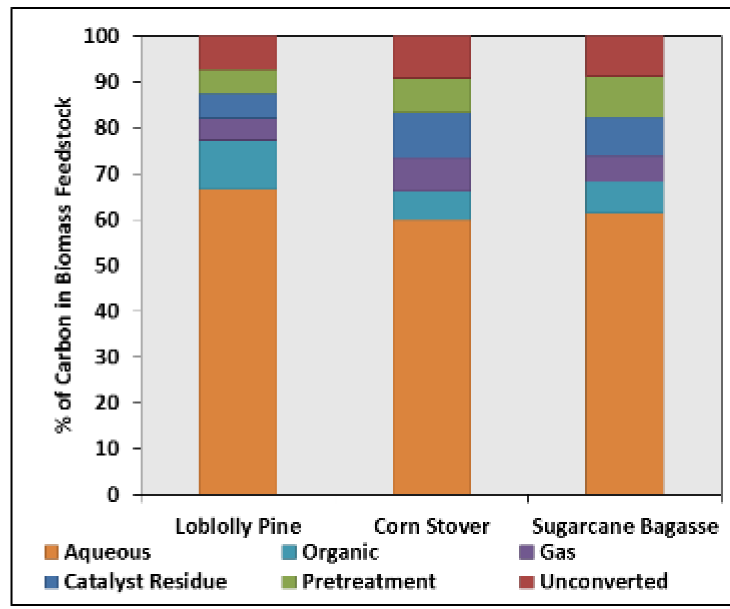


Full Biomass Utilization

-Effectively convert 100% of the biomass carbon (C_5 & C_6 sugars as well as lignin)

-BioForming® technology can handle a broad range of oxygenates

-Primary concern is inorganic ash affecting catalyst lifetime and stability



Feedstock Flexibility

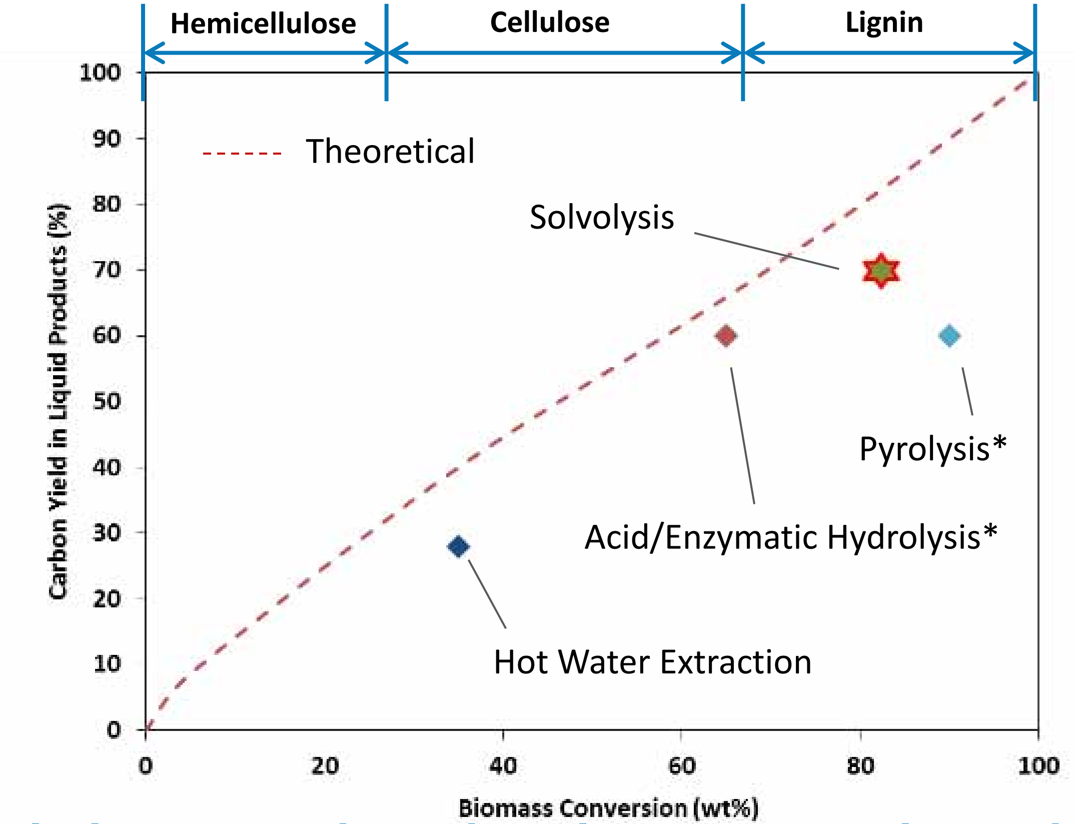
-Each biomass species has distinct differences in their carbohydrate and lignin profiles

-Solvolysis has the ability to solubilize each portion of the biomass under moderate conditions

2 – Approach (Technical)
Summary

- Overall Technical Approach
  - This project utilizes Virent's Solvolysis and BioForming® technologies to deconstruct lignocellulosic biomass into soluble intermediates for catalytic conversion to an aromatic rich liquid fuels.
  - Feedstocks - Loblolly Pine, Corn Stover, Sugarcane Bagasse
  - Products - Gasoline Range Hydrocarbons with a focus on Aromatic Chemicals
- Critical Success Factors
  - Feedstock Supply Chain – Economic collection and delivery of lignocellulosic biomass at a commercial scale
  - Biomass Pretreatment – Reduction of inorganic species known to be catalyst poisons
  - Biomass Deconstruction – Total biomass utilization, including lignin, maximizing carbon yields suitable for catalytic upgrading
  - Catalyst Lifetimes – Demonstrate stability and lifetimes utilizing a lignocellulosic feedstock
  - Economics – Improve capital and operating cost of biomass to liquid fuel process, reducing the overall product costs
- Potential Challenges
  - Feedstock Selection and/or advance pretreatment strategies for reduction of inorganic species without sacrificing convertible carbon
  - Improve yields of liquid fuel through utilization of lignin in addition to carbohydrates, catalyst development and process optimization
  - Demonstrate scalability of biomass digestion and full system integration with BioForming® catalytic technologies.
  - Feedstock flexibility

2 – Approach (Management)
Critical Success Factors



Solvolysis Compared to Other Biomass Processing Technologies

***Illustrative result shown based on literature results for conventional pyrolysis and hydrolysis.**

-Wyman C, Balan V, Dale B, Elander R, Falls M, Hames B, et al. Comparative data on effects of leading pretreatments and enzyme loadings and formulations on sugar yields from different switchgrass sources Bioresource Technology 2011; 102(24): 11052 - 11062.

-Elliott D, Iisa K. Core pyrolysis research and development: Thermochemical conversion platform review. [Internet]. 2011 [cited 2013 January 8]. Available from: http://obpreview2011.govtools.us/Thermochem/.

2 – Approach (Management) (Market/Business Challenges)

Business Risk	Mitigation Strategy
Biomass Price Escalation and Sourcing	Continue to work with groups like INL to determine costs of harvesting biomass. Continue to work on improving yields to lower effect of biomass price volatility on final fuel product.
Prolonged Depression of Crude Oil Prices	Strive to be the low cost producer of cellulosic hydrocarbon biofuels. Optimize byproduct streams for use as chemical/petrochemical to increase co-product value.
Financing	Financing will be determined by projected cost of production, profitability, capital risk, and optimal site location.
Policy Uncertainty	Continue promoting efforts and participation in groups like Advanced Biofuels Association (ABFA), Biotechnology Industry Organization (BIO) and others.
Emerging Competitive Technologies	Monitor competitive landscape and continue to expand IP portfolio.
Prolonged Elevated NG Prices	Continue to increase liquid fuel yields in order to minimize hydrogen cost. Optimize engineering to make sure hydrogen is effectively used.

3 – Technical Accomplishments
Milestones

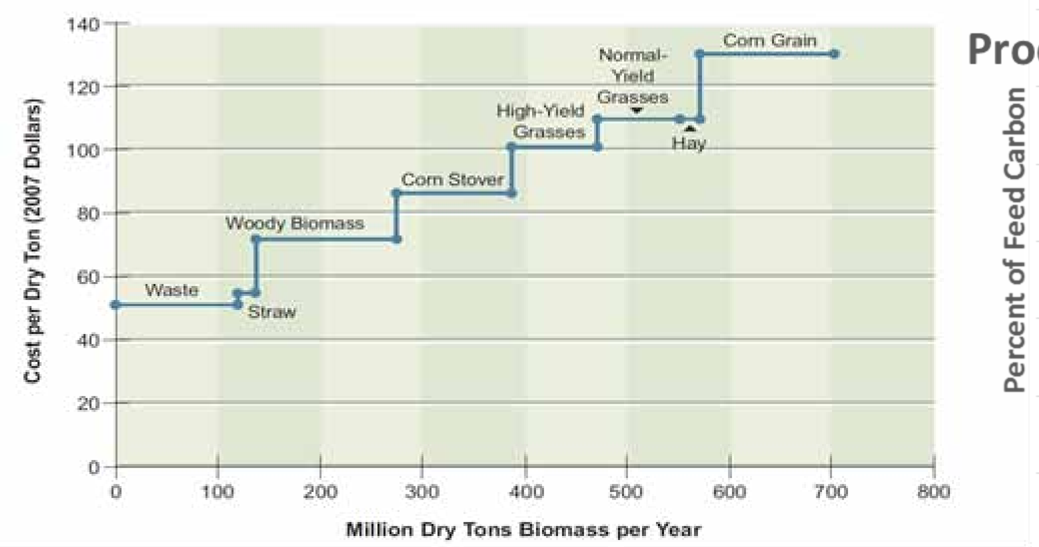
- Biomass Solubilization
  - √ Achieve >90% biomass solubilization
  - √ Achieve >80% yield of oxygenates from carbohydrate fraction with 95% biomass solubilization
  - √ Build and commission a continuous deconstruction unit maintaining yield and conversion of batch systems
- Upgrading Biomass Intermediates to Aromatic Fuels and Chemicals
  - √ Identify and implement safety upgrades for increased aromatics generation
  - √ Achieve 50% improvement in selectivity to aromatics using model feed
  - √ Demonstrate 50% improved selectivity to aromatics using cellulosic feed
  - √ Fully characterize and validate a catalyst lifetime of at least 3 months using cellulosic feed
- Project Directives and Process Development
  - √ Downselect to a single feedstock with most promising deconstruction path to Aromatics
  - – Identify optimal configuration and operating conditions for maximizing aromatics production
  - – Achieve a theoretical Solvolysis catalyst lifetime of at least 1 year through accelerated testing
  - – 2000 hr run with theoretical catalyst lifetime of 1 yr
  - – Develop TEA model for deconstruction process

3 – Technical Accomplishments
Feedstock Downselect Milestone

Woody Biomass Advantages

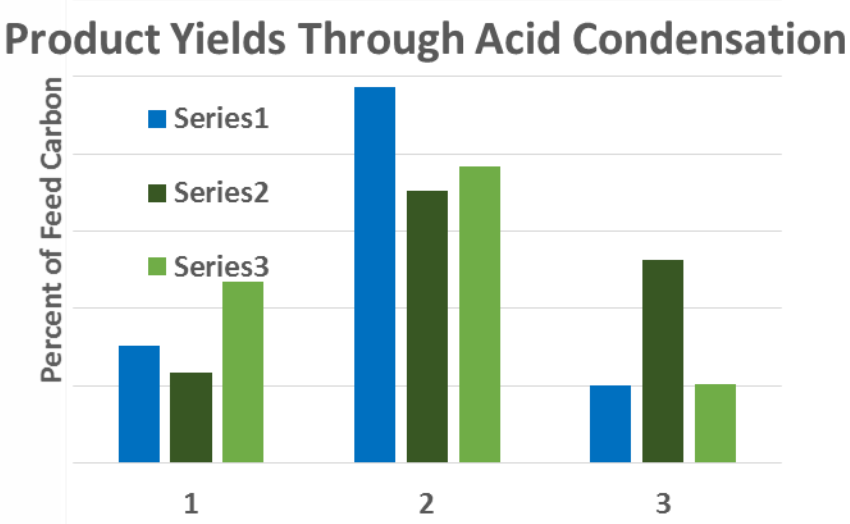
-CHNO Analysis & Inorganic Ash Concentration
-Biomass effect on product composition
-Feedstock Cost
-Feedstock Supply Chain

Variable (%wt)/Feedstock	Loblolly Pine	Corn Stover	Sugarcane Bagasse
Moisture	7.97	10.25	5.8
Ash	0.7	4.25	10.03
Carbon	51.1	46.44	45.77
Hydrogen	5.94	5.59	5.47
Oxygen	42.22	43.33	38.7
Nitrogen	<0.5	<0.5	<0.5
Sulfur	<0.05	0.065	<0.05
Chloride	0.0361	0.315	0.0266

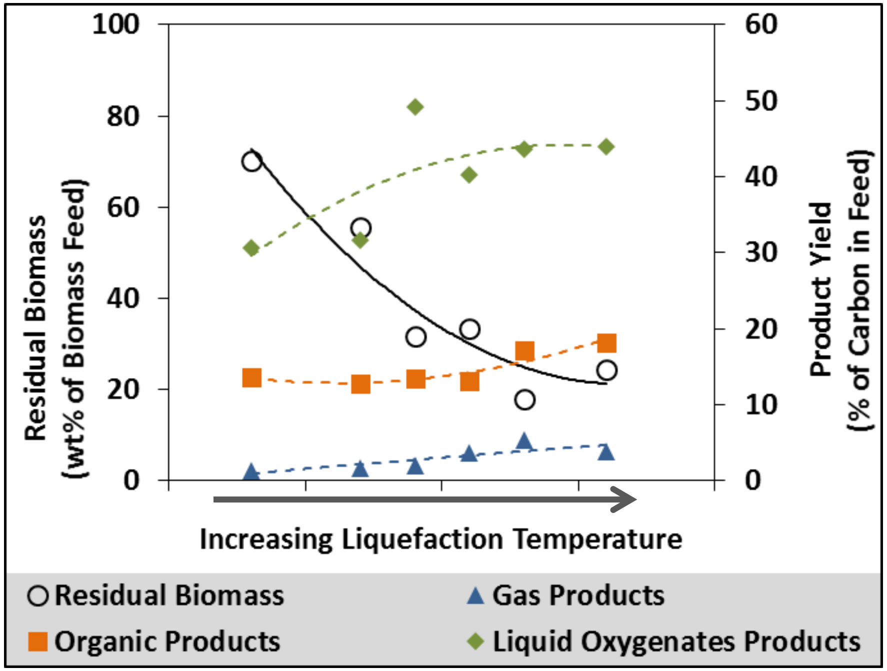


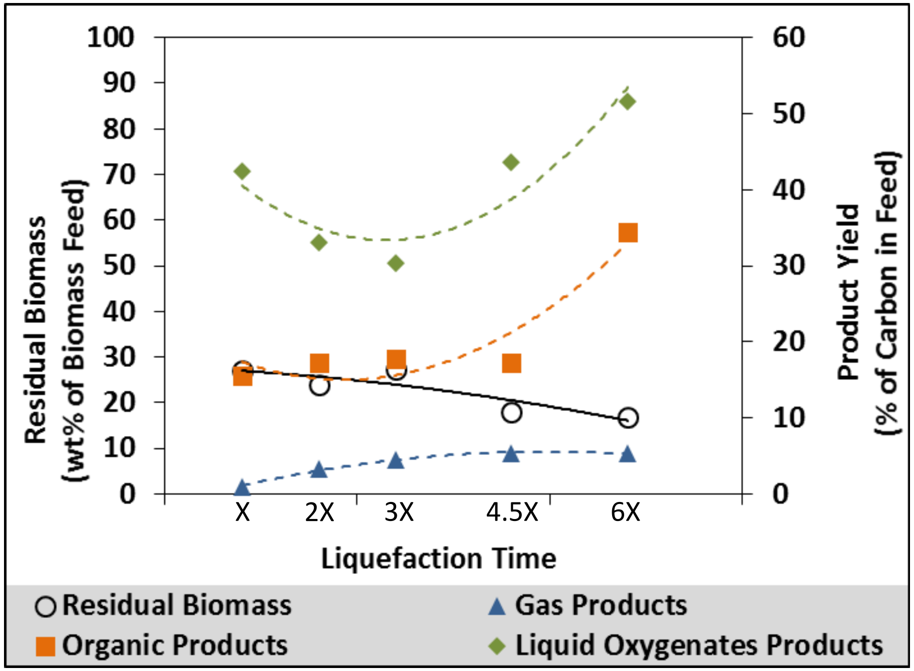
Supply costs of various biomass feedstocks

Source: Liquid Transportation Fuels from Coal and Biomass (National Academies of Sciences and Engineering). Dry tons are in short tons.



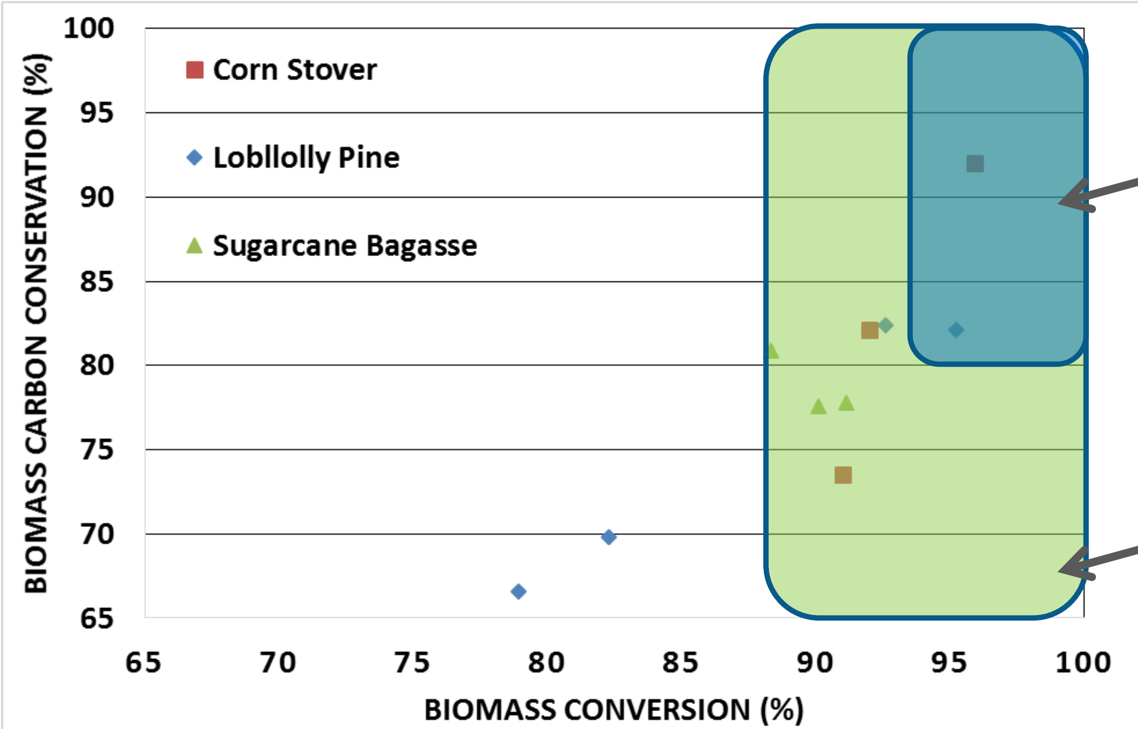
3 – Technical Accomplishments
Solvolysis Condition Optimization





Investigation of liquefaction time, temperature and flow characteristics have allowed for high conversion (>95%) and improved carbon recovery (>80%) into organic and liquid oxygenated products

3 – Technical Accomplishments
Solvolysis Conversion VS Conservation



Completed Milestone
>95% Biomass Solubilization with >80% Yield of Oxygenates

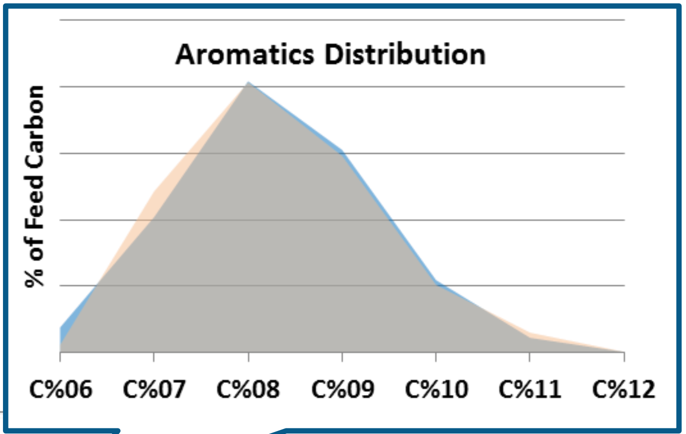
Completed Milestone
>90% Biomass Solubilization

Biomass Conversion – weight % of liquefied biomass

Biomass Carbon Conservation – weight % of carbon retained in the liquid phase for condensation to fuels and chemicals (Losses to the gas phase and char formation)

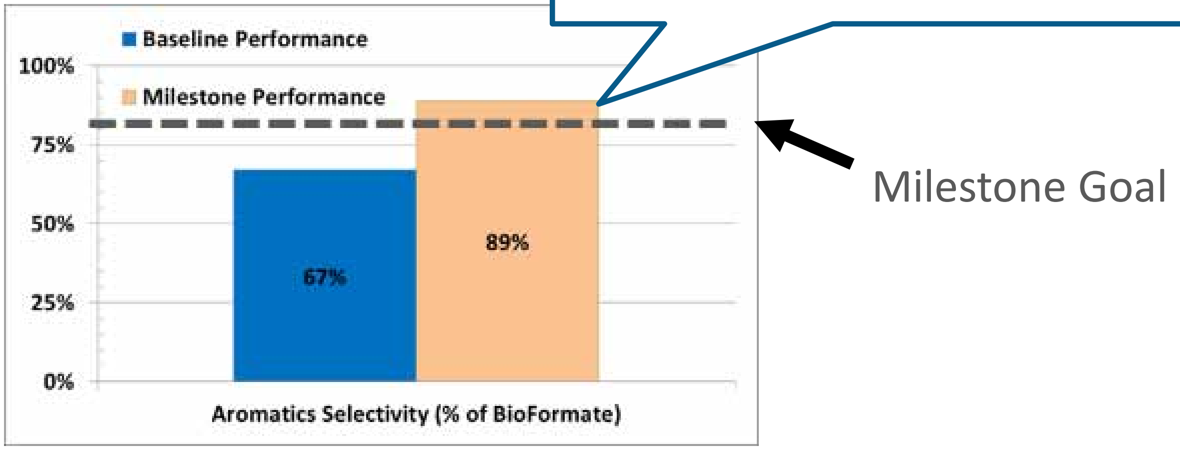
3 – Technical Accomplishments
Acid Condensation Selectivity Improvement Milestone

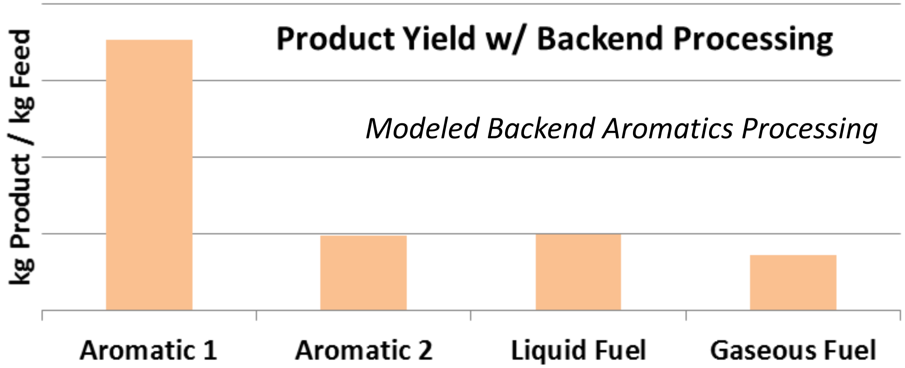
Acid Condensation Feed	BioFormate Yield (% of Feed Carbon)	Aromatics Yield (% of Feed Carbon)	Aromatics Selectivity (% of BioFormate)	Milestone Goal of Aromatics Selectivity (% of Bioformate)
Model Feed	70%	48%	68%	84%
Solvolysis Products	69%	46%	67%	84%



Goals:

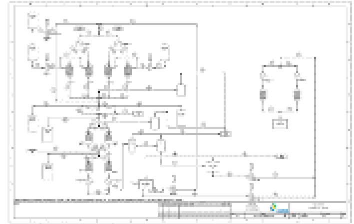
- 50% Improvement in Aromatics Selectivity
- Characterization of Catalyst following completion of work
- **Milestones Completed 10/30/2014**



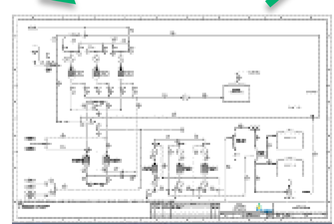


3 – Technical Accomplishments

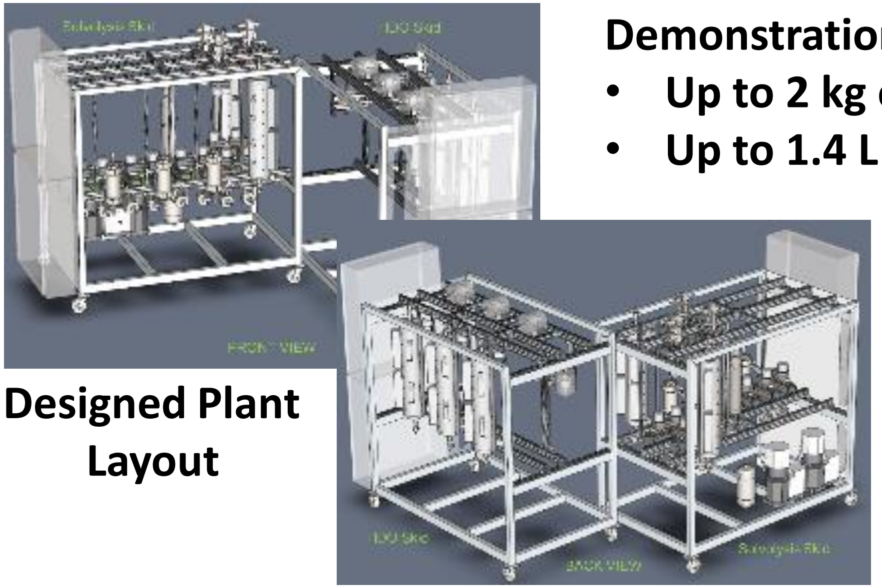
Design, Build & Commissioning a Fully Continuous Deconstruction System



Design Vision → Design and Operation Philosophy → Initial Design → Design Review → PHA → Build



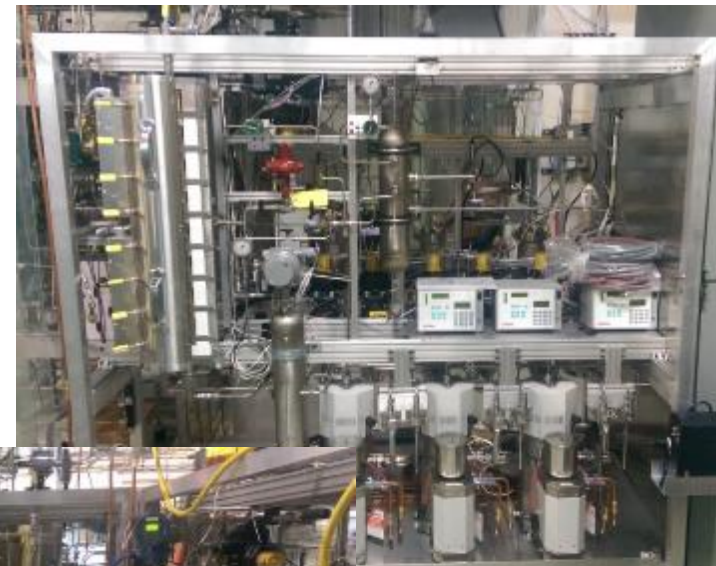
3 – Technical Accomplishments
Completed Demonstration Unit

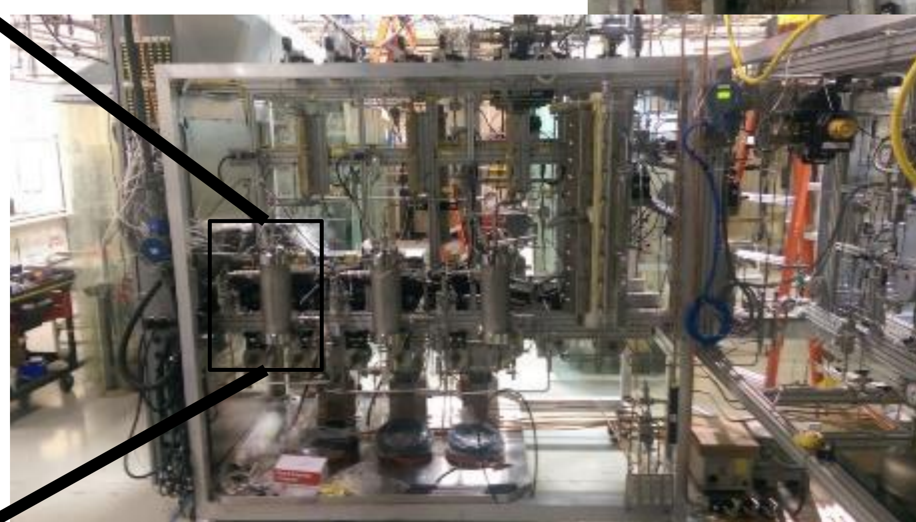


Designed Plant Layout

Demonstration Unit Scale

- Up to 2 kg of biomass per day
- Up to 1.4 L of BioFormate® per day





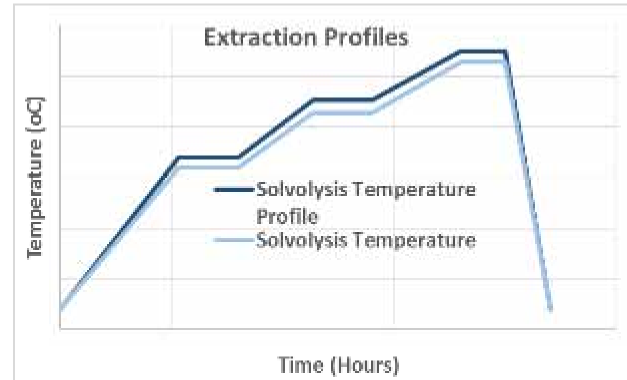
Built Plant Layout

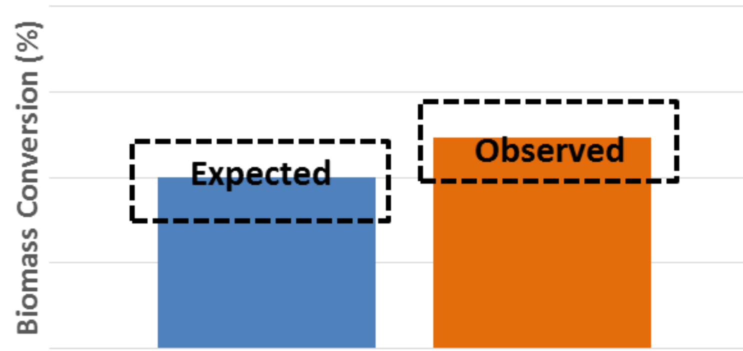
3 – Technical Accomplishments
Demonstration Unit Results

- **Unit is Fully Operational**
  - Allows for Comparison of Solvolysis at Various Scales (g/day to kg/day of biomass)

- **Generating Data for TEA Model**
  - Validate model with data
  - Evaluate commercial costs (equipment, heat loads, etc.)
  - Utilize model sensitivity analysis to identify areas to focus research efforts

- **Optimize System Conditions**
  - Identify optimal configuration and conditions for maximum product yields





4 – Relevance

Contributes to meeting the platform goals and objectives of the BETO Multi-Year Program Plan by:

- Developing feedstock specifications and processing systems that accommodate feedstock variability and are optimized for convertibility.
- Developing technologies for converting biomass into bio-oil or syngas intermediates for subsequent upgrading into fuels and chemicals.
- Validating the sustainability and technical improvements of the integrated conversion technologies.
- Develop, refine and utilize life-cycle and process engineering/TEAs for priory and alternative thermochemical conversion routes.

Applications of the expected outputs in the emerging bioenergy industry

- Results from this project provide technical viability of combining a thermochemical conversion technology frontend with a chemical (catalytic) conversion technology to generate "direct replacement" hydrocarbons from a lignocellulosic feedstock.
- Process is showing it can utilize a wide range of feedstock components and is feedstock flexible.
- Process is showing its ability to scale the technology and progression along the TRL path.

5 – Future Work

Milestone Title	Description	Deliverable	Estimated Completion
Acid Condensation Catalyst Lifetime Improvements	Achieve theoretical catalyst lifetime of at least 1 year through accelerated testing	Report the results in the quarterly report	6/2015
Process Optimization	Identify optimal configuration and operating conditions for maximizing aromatics production	Report the results in the quarterly report	5/2015
Solvolysis – Acid Condensation Demonstration Run	2000 hour run with theoretical catalyst lifetimes of 1 year	Milestone report submitted in conjuncture of quarterly report	9/2015
Catalyst Characterization	Complete catalyst characterization of the catalysts used in the demonstration run, including Solvolysis and Acid Condensation	Catalyst characterization in the final project report	9/2015
TEA	Updated process simulation and cost models incorporating technical achievements	TEA and LCA reported in the final project report	9/2015
Project Completion and Final Project Report	Final project report including project summary, all milestone progress, detailed technical summary and TEA updates.	Final project report	10/2015

Summary

1. Overview
   - Convert lignocellulosic feedstocks to fuels and high value aromatic chemicals
   - Utilizes unique solvents created by the stabilization process to liquefy lignocellulosic biomass and integrate with Virent's BioForming® Catalytic Upgrading
2. Approach
   - Progress technology and demonstrate scalability of a fully continuous process
3. Technical Results
   - >95% liquefaction possible
   - >80% conservation of carbon intermediates for condensation to fuels and chemicals
   - Condensation produces an aromatic rich hydrocarbon product
4. Relevance
   - Demonstrate technical and economic viability of process
5. Future Work
   - Demonstrate fully integrated process, improve catalyst lifetimes, process optimization, evaluate scalability and technoeconomics,

Additional Slides

Responses to Previous Reviewers' Comments

- Benzene Generation/Safety
  - Proper safety procedures were documented along with construction of engineering controls for safe generation and handling of benzene as well as other hazardous chemicals.
- Project Outlook is At Risk to Fall Behind Schedule
  - A one year, no cost, time extension was granted to allow for completion of project goals and milestones.
- Major Hurdles Exist In: Feedstock, Catalyst Poisoning, Inorganic Ash Removal and Carbon Retention
  - Feedstock was downselect to loblolly pine to reduce total ash into the system and eliminate need for feedstock pretreatment increasing carbon yields.
  - Catalyst lifetime concerns still exist however several improvements are being reviewed to extend lifetime and stability. Minimization of ash within the system has the largest impact and cleanup of products prior to stabilization has shown to prevent >90% of the ash from reaching the catalysts.
  - Optimization of process conditions to maximize biomass carbon utilization and overall process yields.

Publications, Patents, Presentations, Awards, and Commercialization

- Qiao, Ming; Woods, Elizabeth; Myren, Paul; Cortright, Randy; and Connolly, Sean; Patent Application PCT/US2013/0318258 Solvolysis of Biomass to Produce Aqueous and Organic Products.
- Qiao, Ming; Woods, Elizabeth; Myren, Paul; and Cortright, Randy; Patent Application PCT/US2013/0019859 Solvolysis of Biomass and Stabilization of Biomass Hydrolysate.