# Catalytic Upgrading of Thermochemical Intermediates to Hydrocarbons:

## Conversion of Lignocellulosic Feedstocks to Aromatic Fuels and High Value Chemicals

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Technology Area Review: Thermochemical Conversion

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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**
  - Deconstruction 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: 100%

## 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 | $610,834 | $1,043,133 | $1,001,880 | $1,244,965 |
| Virent Cost Share | $500,983 | $855,544 | $821,710 | $1,021,083 |

## 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 Management

## Project Management

- Project Management Plan and Project Work Plan
- Weekly team meetings
- Monthly Update calls with the DOE
- Quarterly/Final Reporting
  - Technical, Milestones, Financial
- Milestone reports
- Internal Stage Gate prior to Pilot Plant Build
- Peer Reviews (2013, 2015)

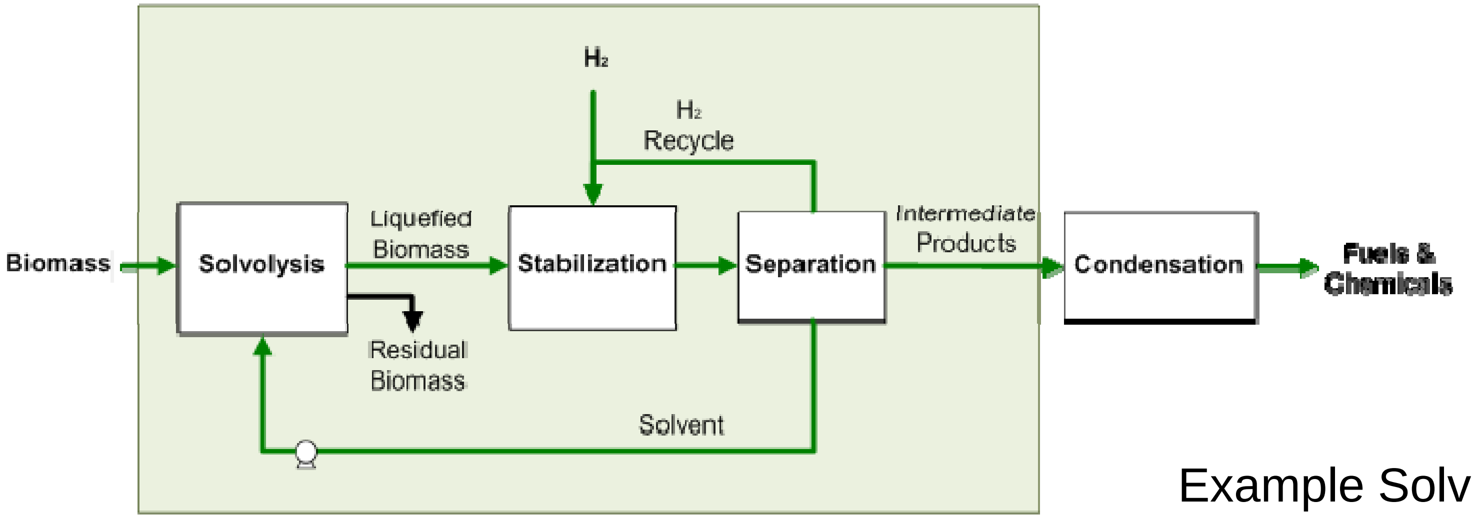
# 2-Approach Management

## Milestones and Deliverables

| Task | Milestone Description | Deliverables |
|---|---|---|
| Fundamental R&D | Solubilization of sugar cane bagasse, corn stover, and wood residuals | Achieve 90% conversion for each feed |
| Fundamental R&D | Complete safety upgrades for aromatics generation | Identified and installed necessary laboratory safety upgrades to allow generation of higher concentrations of benzene |
| Fundamental R&D | Improve selectivity to aromatics with model feeds within the COTA process | Achieve 50% improvement over the baseline in selectivity to aromatics using model feed |
| Fundamental R&D | Improve COTA selectivity to aromatics with cellulosic feedstocks | Demonstrated 50% improvement in selectivity to aromatics using cellulosic feed with an expected catalyst lifetime of at least 3 mos. |
| Process Development | Down select of process configuration and feedstock | Down select to a single feedstock with most promising deconstruction path to Aromatics for use in years 2 and 3 |
| Process Development | Improve Solubilization/HDO Process | Achieve 80% yield of volatile oxygenates from carbohydrate fraction of biomass and 95% biomass conversion |
| Project Management | Hold a review to assess project progress and determine scope and funding revisions if necessary | Go-No-Go decision with report detailing supporting information |
| Process Development | Complete Solubilization/HDO Pilot Plant Upgrades | Commission upgraded biomass deconstruction pilot plant using biomass feed to produce hydrolysate |
| Process Development | 2000 hour Demonstration Run | 2000 hour-run with theoretical catalyst lifetime of at least 1 year |
| TEA/LCA | Techno-economic and Life Cycle Analysis | Updated process simulation, cost models, and life cycle models incorporating technical achievements. |
| Project Management | Project Management & Reporting | Manage communication, manage advisor committee and reporting throughout duration of the project. |

# 2 – Approach (Technical)

## Overall Technical Approach



Biomass

Solvolysis

Liquefied Biomass

Residual Biomass

$H_2$

$H_2$ Recycle

Stabilization

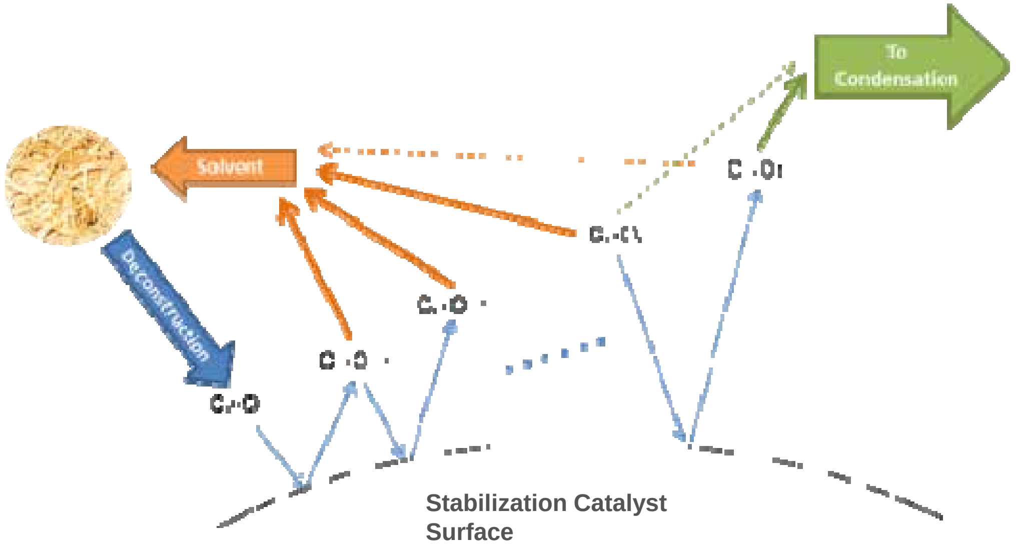
Separation

Solvent

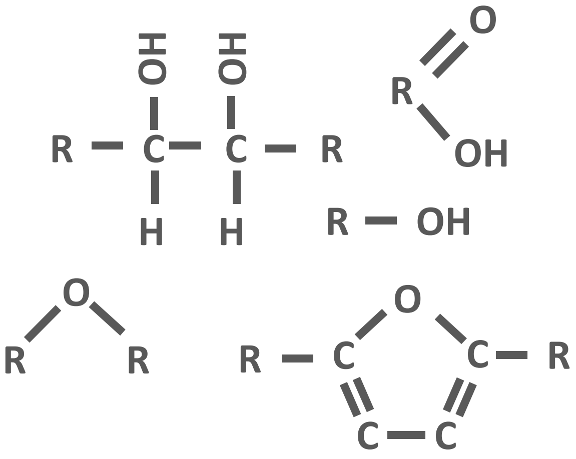
*Intermediate* Products

Condensation

**Fuels & Chemicals**

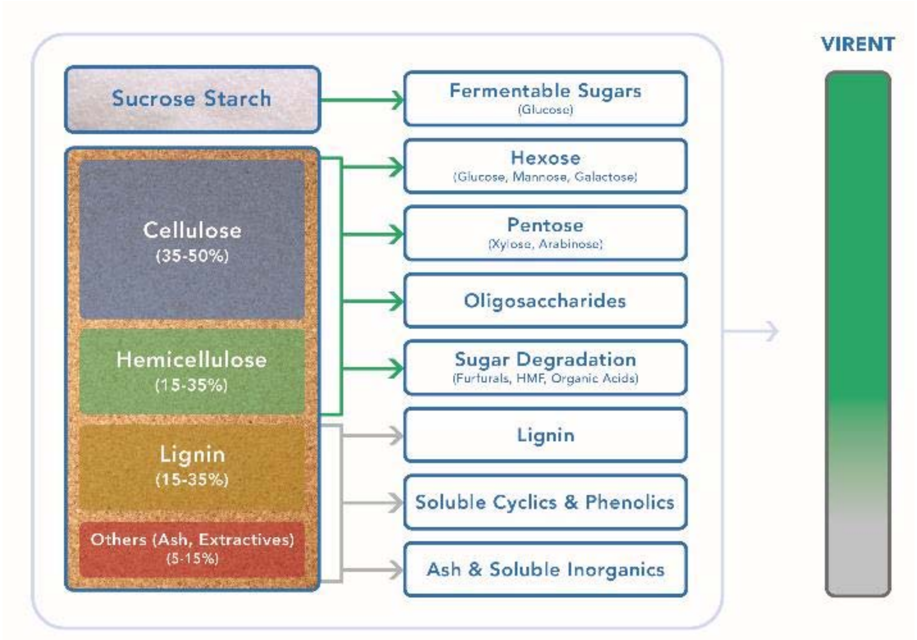


Example Solvent Compounds



-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 the biomass carbon ($C_5$ & $C_6$ sugars as well as lignin)

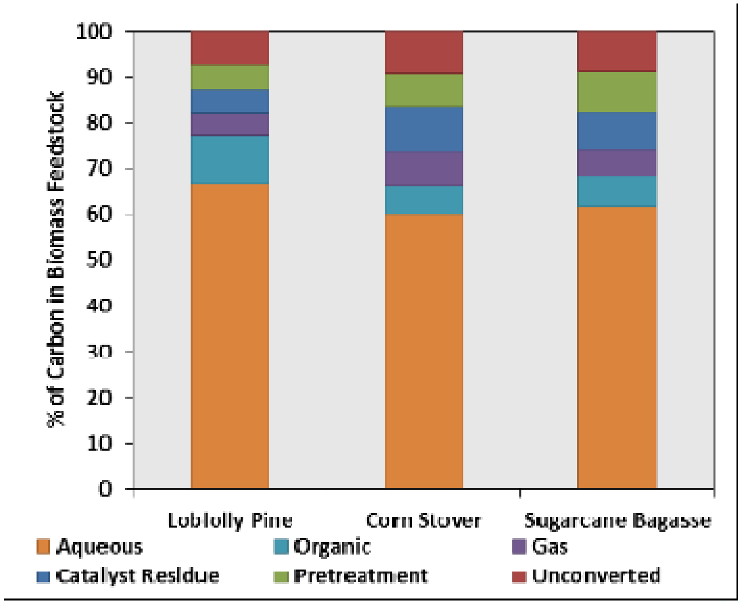
-BioForming® technology can handle a broad range of oxygenates

-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



*Similar carbon removal from biomass for forward processing (aqueous and organic) from three different feedstocks*

# 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

# 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**

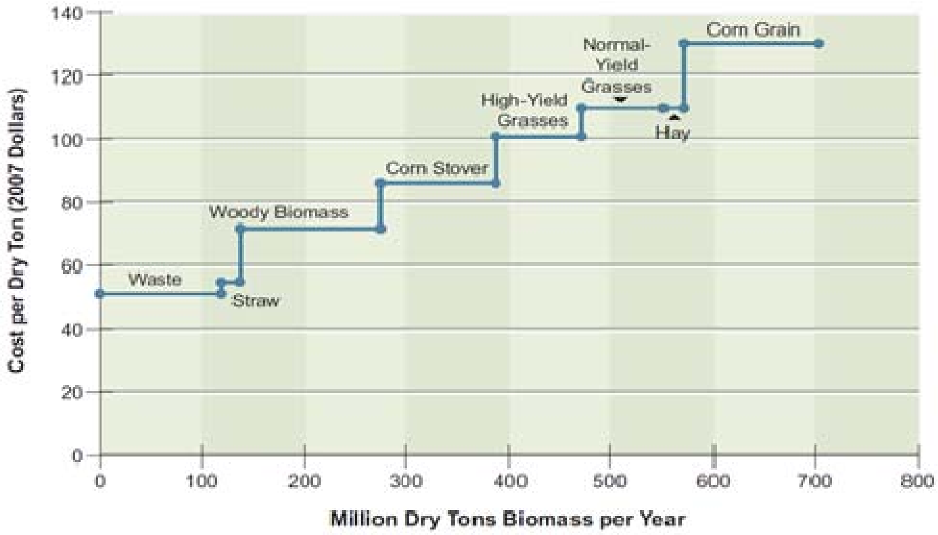
-CHNO Analysis & Inorganic Ash Concentration

-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 |

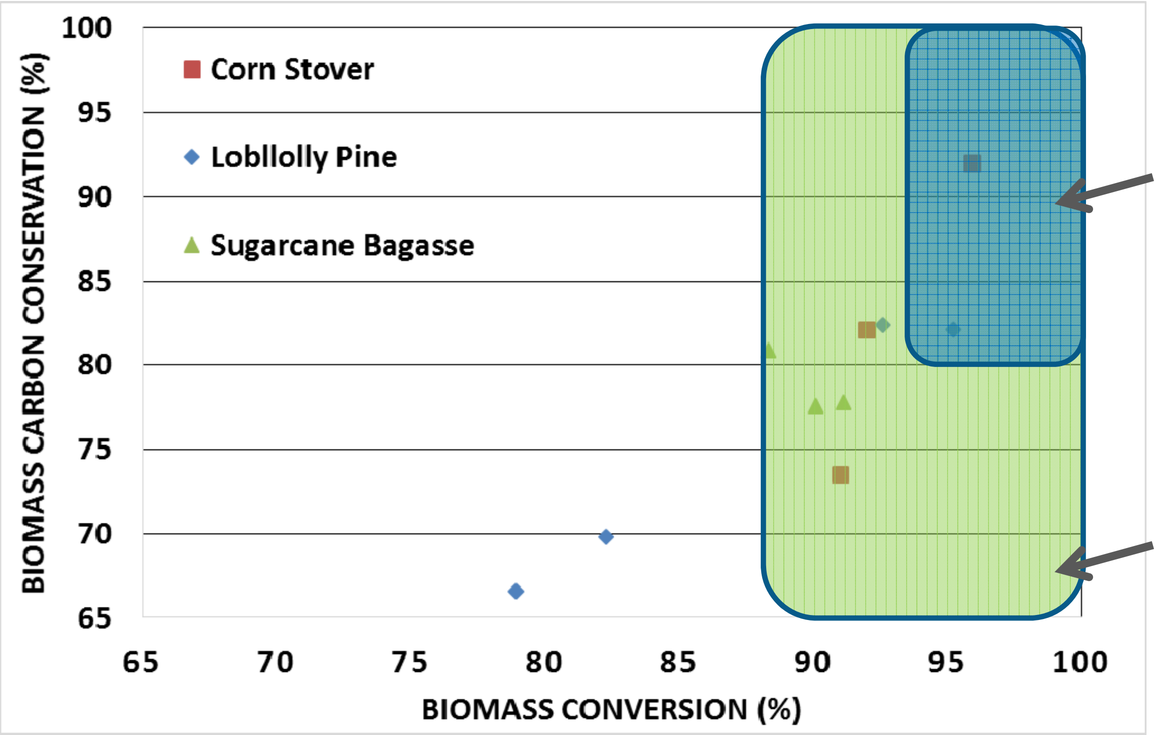


Supply costs of various biomass feedstocks

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

# 3 – Technical Accomplishments

## Solvolysis 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

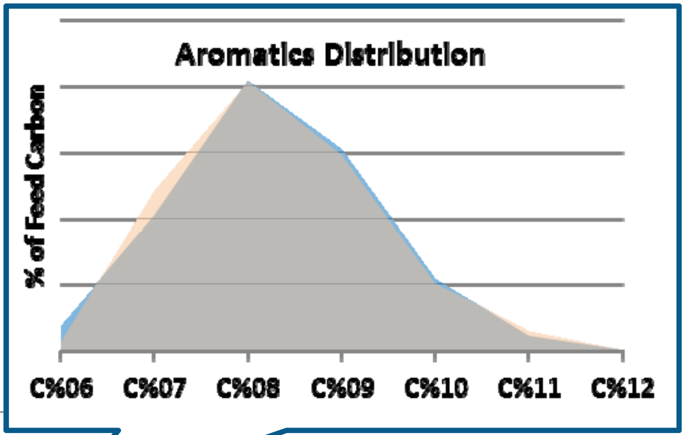
## Acid Condensation Selectivity Improvement Milestone

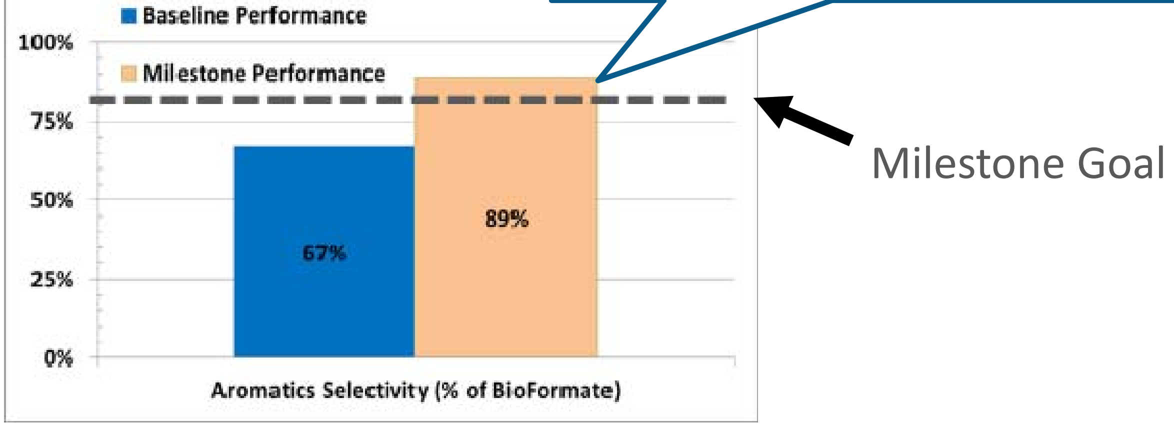
| Acid Condensation Feed | BioFormate Yield (% of Feed Carbon) | Aromatics Yield (% of Feed Carbon) | Aromatics Selectivity (% of BioFormate) | Milestone Goal of Aromatics Selectivity (% of Bioformate) |
|---|---|---|---|---|
| Model Feed | 70% | 48% | 68% | 84% |
| Solvolysis Products | 69% | 46% |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

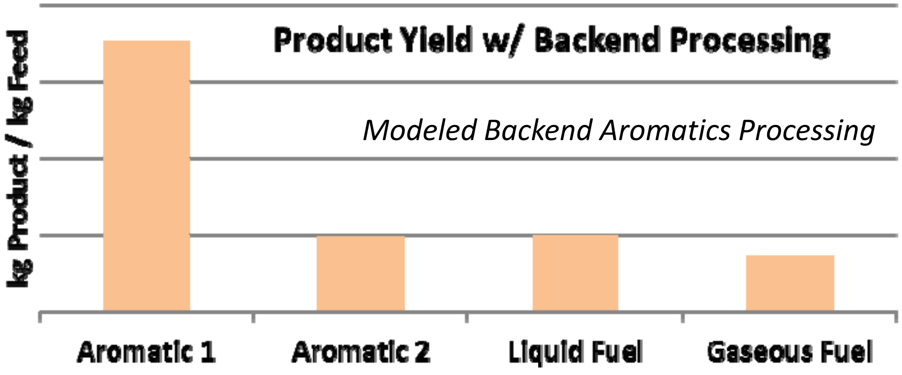
*Model feeds displayed similar performance to solvolysis product feed*

**Goals:**

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

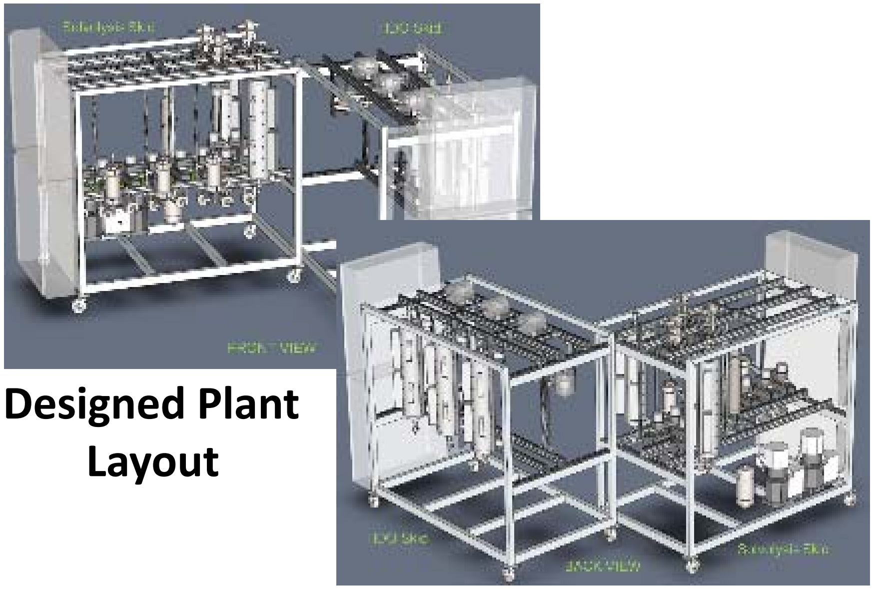




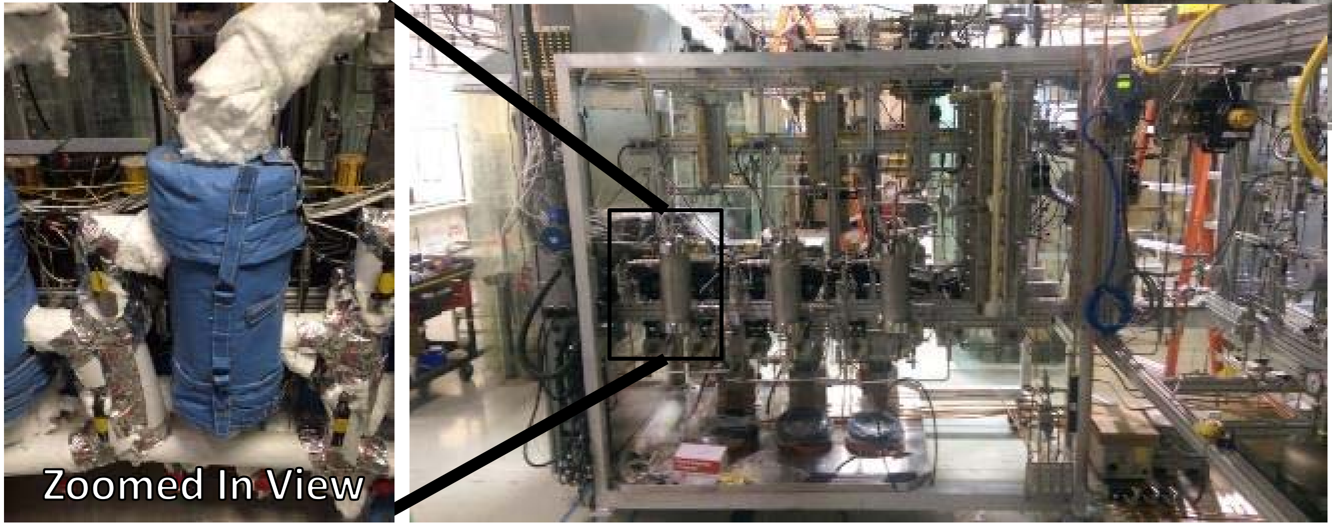


# 3 – Technical Accomplishments

## Design, Build & Commissioning a Fully Continuous Deconstruction System



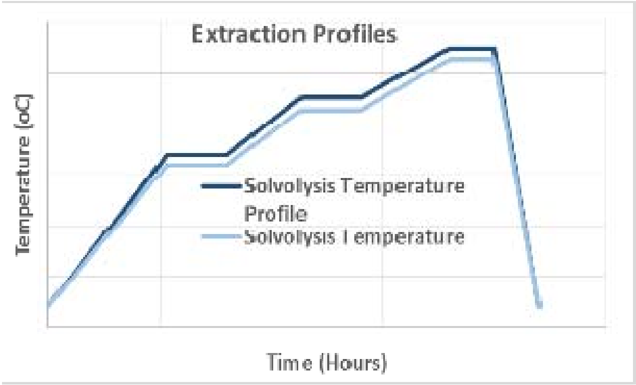
Designed Plant Layout

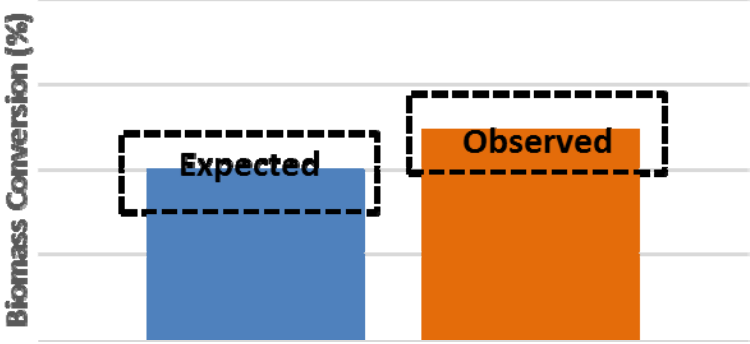


Built Plant Layout

# 3 – Technical Accomplishments
## Demonstration Unit Results

- **Unit is Fully Operational**
  - Allowed for Comparison of Solvolysis at Various Scales (g/day to kg/day of biomass)
- **Generating Data for TEA Model**
  - Validated model with data
  - Evaluated commercial costs (equipment, heat loads, etc.)
  - Utilized model sensitivity analysis to identify areas to focus research efforts
- **Optimize System Conditions**
  - Identified optimal configuration and conditions for maximum product yields





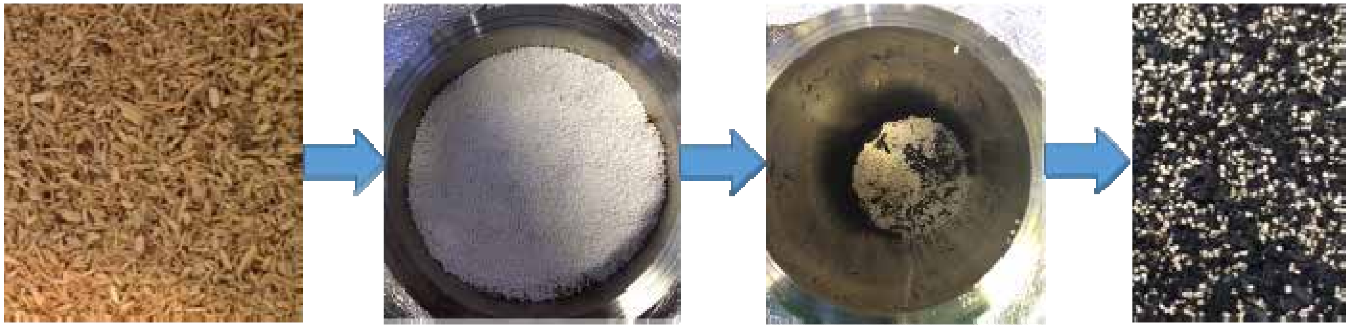


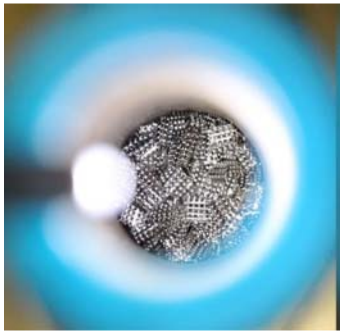
Photo from L to R: Fresh loblolly pine biomass, fresh biomass and co-loaded reactor, reactor post solvolysis extraction, remaining biomass and co-load

# 3 – Technical Accomplishments

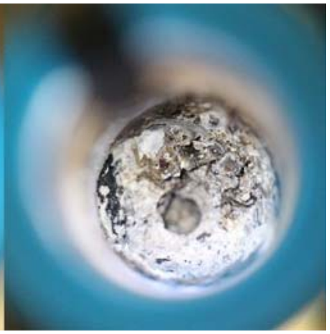
## Demonstration Unit Stability Run

**Operated on-stream >2,000 hours with integrated process**

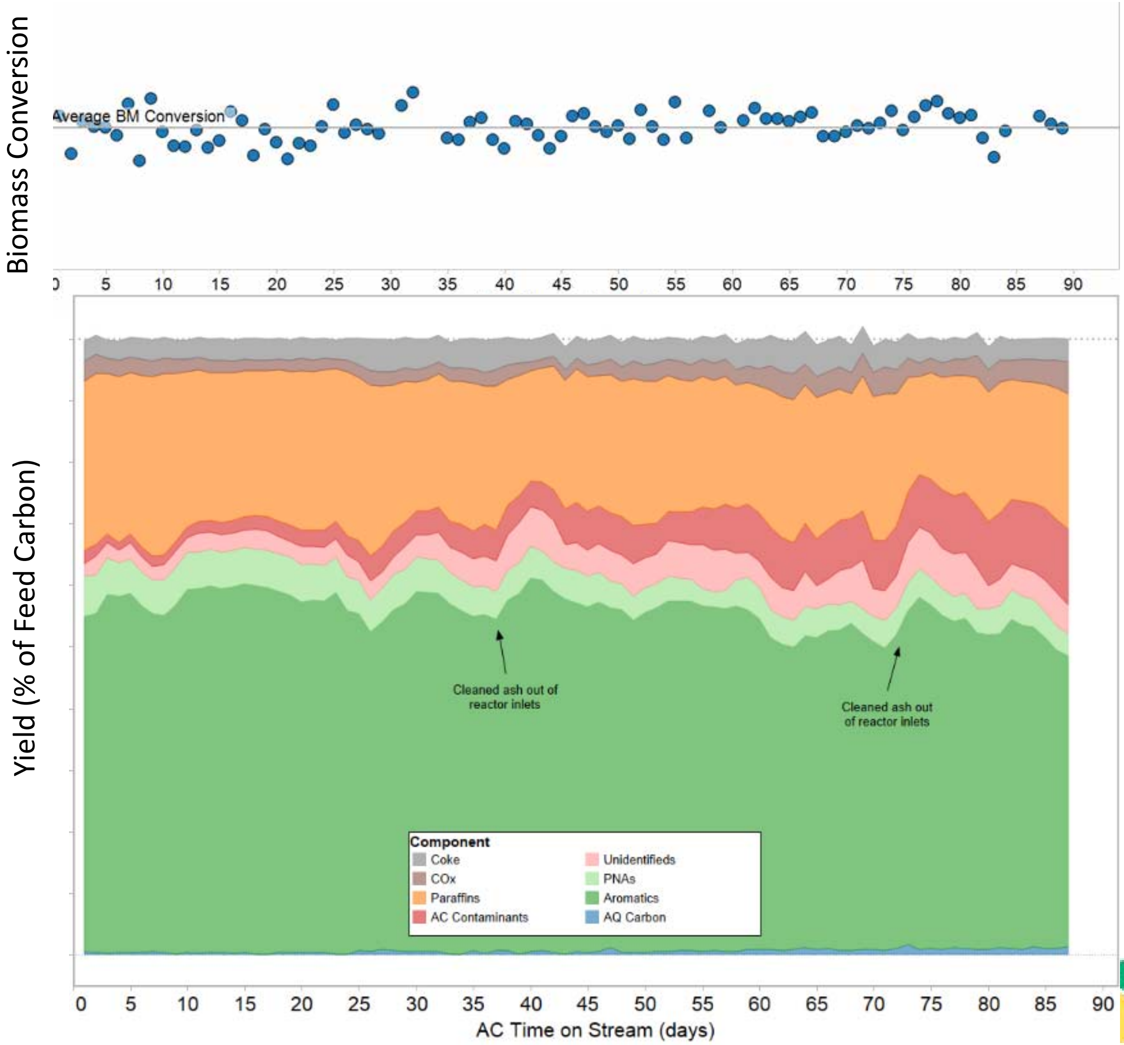
- Stable system operation
- Total system uptime >92%
- Biomass deconstruction and HDO section required shutdown to remove carbon buildup in tubing
- Acid condensation (COTA) shutdown required to remove ash from reactor inlet



Clean preheater



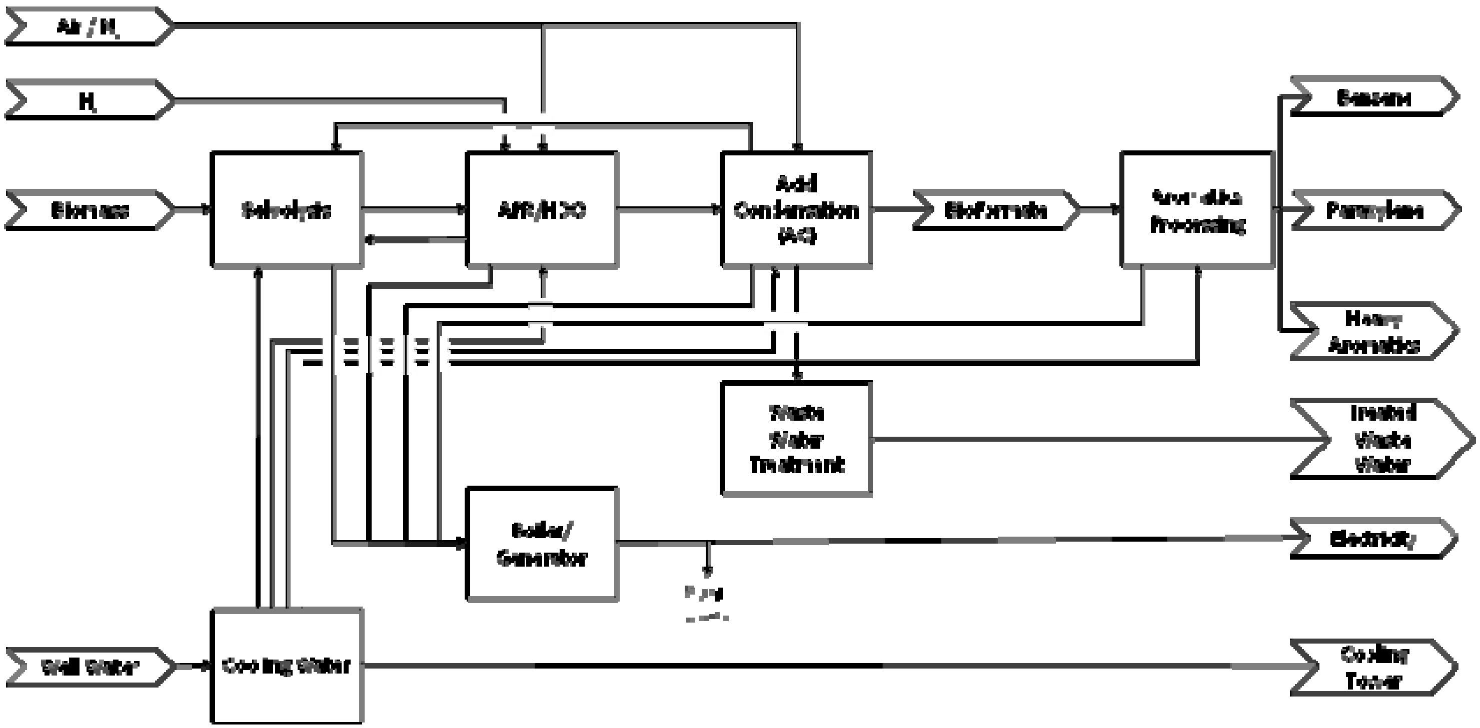
Ash build-up



# 3-Technical Accomplishments Engineering, TEA, LCA

Integrated Demonstration Unit data basis for Aspen Plus Design

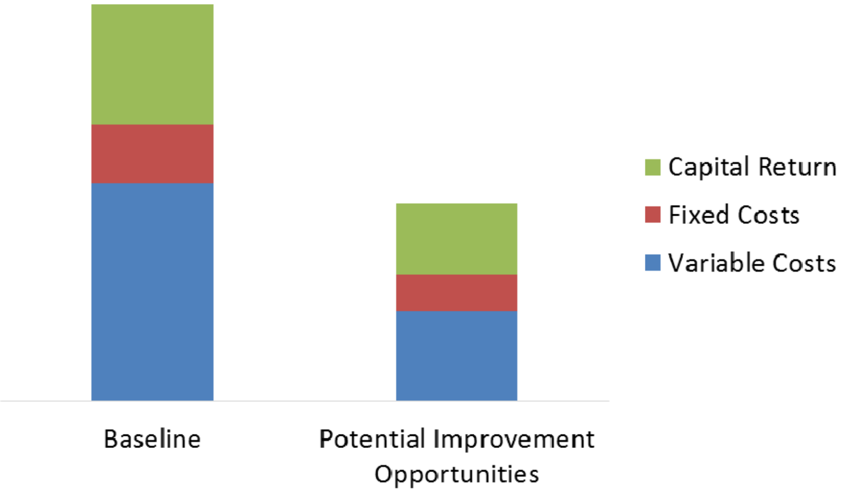
Basis for Equipment sizing, capital and operating cost estimates and life cycle analysis.



# 3-Technical Accomplishments
# TEA & LCA Results

**TEA**

- 2000 Metric Tons/Day loblolly pine
- Integrated laboratory data
- Aspen process model
- Sensitivities
  - Overall Process Yield
  - Capex
  - Catalyst Performance



**LCA**

- 2015 GREET.NET
- Aspen process model
- Baseline case of >**90% reduction** versus petroleum baseline
- Sensitivities
  - Overall Process Yield
  - Electricity Grid Mix
  - Hydrogen Source

# 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

- Final Project Close-Out

# Summary

1. Overview
   - Converted lignocellulosic feedstocks to fuels and high value aromatic chemicals
   - Utilized unique solvents created by the stabilization process to liquefy lignocellulosic biomass and integrate with Virent's BioForming® Catalytic Upgrading
2. Approach
   - Progressed 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
   - Demonstrated technical and economic viability of process in 2000 hour demonstration run
   - Identified areas for potential improvement opportunities
5. Future Work
   - Final Reporting

# Additional Slides

# Responses to Previous Reviewers' Comments

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# 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.