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: 3.3.1.10

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 chemicals applications.

- **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 chemicals such as benzene and paraxylene.

Quad Chart Overview

Timeline

- Start – October 2011
- End – October 2014
- Percent complete ~ 25%

Barriers

- **Tt-G: Catalyst Development**
- **Tt-E. Liquefaction of Biomass**
- **Tt-G. Fuel Synthesis**

Budget

- FY11: ($1.92MM / $1.58MM)
- FY12: ($1.25MM / $1.02MM)
- FY13: ($ 827K / $ 678K)
- Funded Years to Date: 1.5
- Average annual funding: $1.3MM

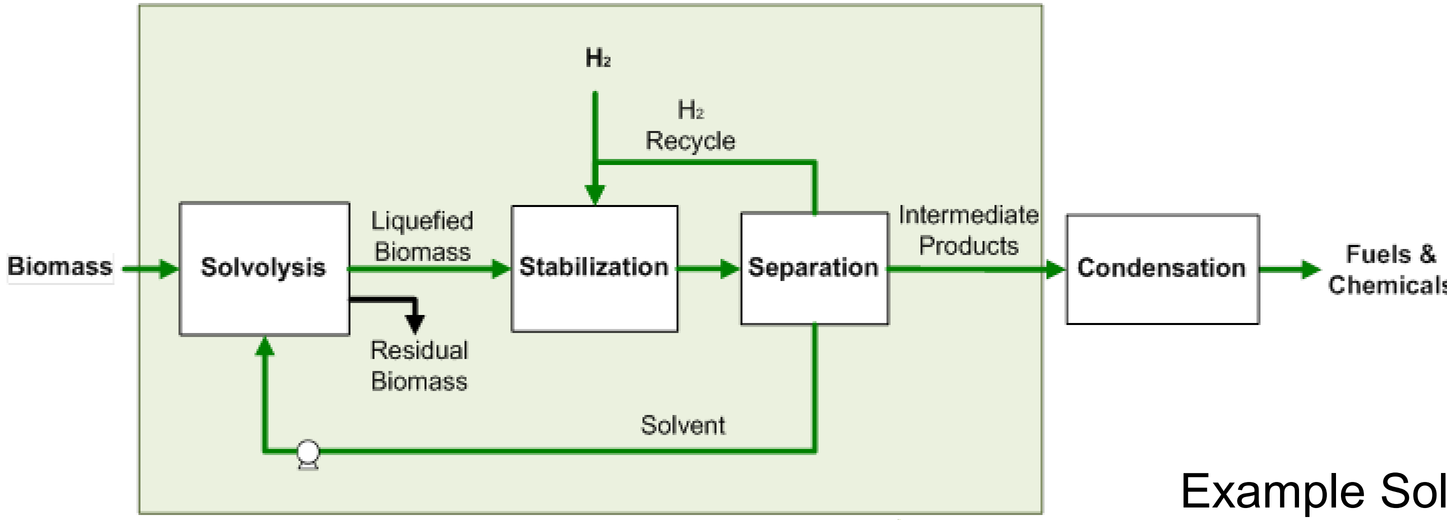
Partners

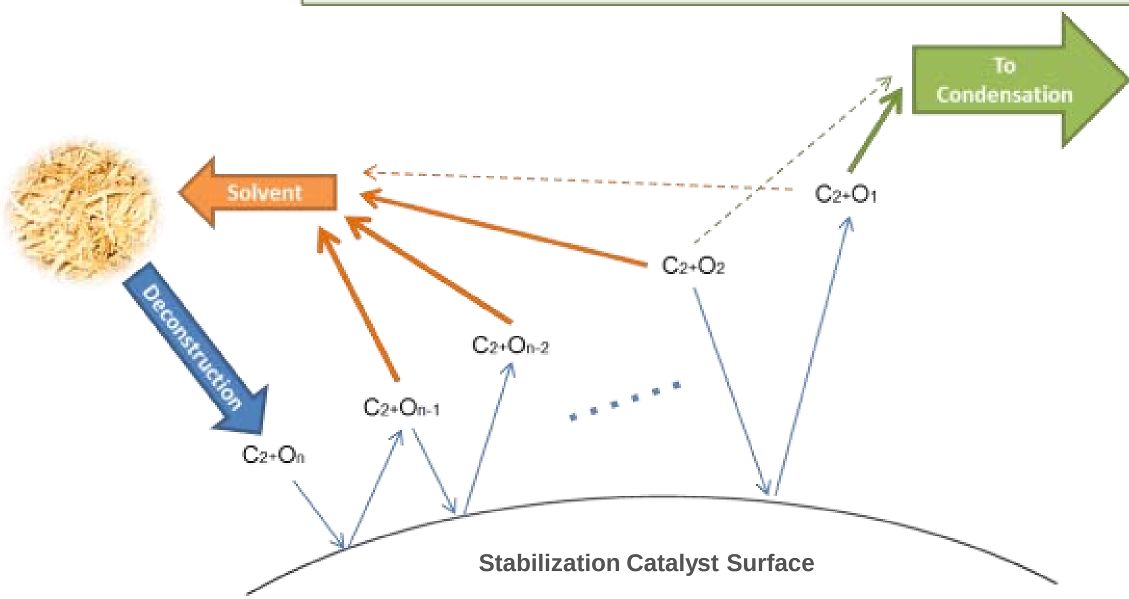
- Feedstock supply: Iowa State University, Catchlight Energy and Louisiana State University AgCenter
- Industry Advisory Committee (Bayer, Catchlight Energy, and The Coca Cola Company)

Project Overview

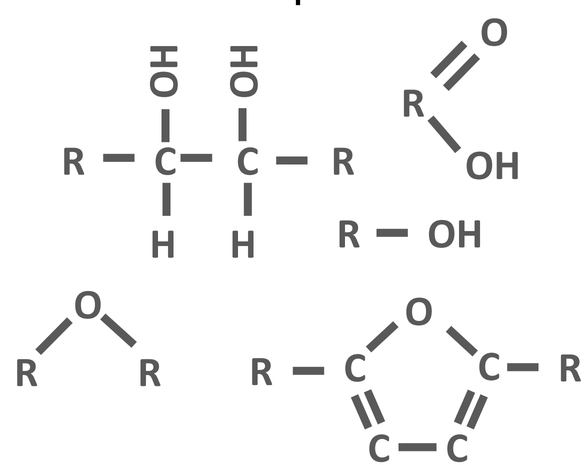
- A differentiating factor of this work is that oxygenated intermediates generated from lignocellulosic feedstocks utilizing Virent's Solvolysis technology are converted to an aromatic-rich hydrocarbon stream using Virent's catalytic condensation process.
- The aromatic-rich product stream from this integrated process can be fractionated to provide aromatics necessary in transportation fuels and high value chemicals. Key objectives include:
  - Demonstrate Virent's Solvolysis Technology is effective for multiple feedstocks:
    - Residual Wood, Corn Stover, Bagasse
  - Demonstrate oxygenated intermediates generated via Virent's solvolysis can be effectively converted to aromatics through condensation.
  - Confirm scale-up viability and economics of integrated process.
  - Demonstrate operability of the fully integrated lab-scale biomass to aromatics process via a 2000 hr lifetime run.

Solvolysis Process Overview



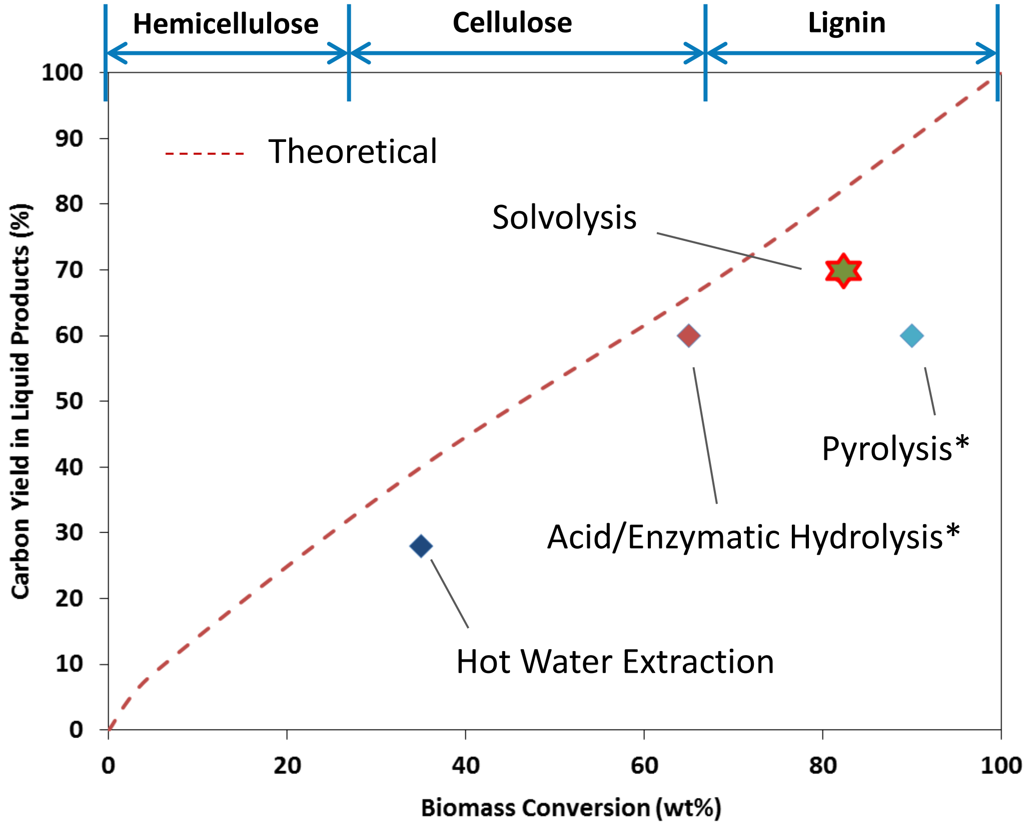


Example Solvent Compounds



-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

Solvolysis Compared to Other Biomass Processing Technologies



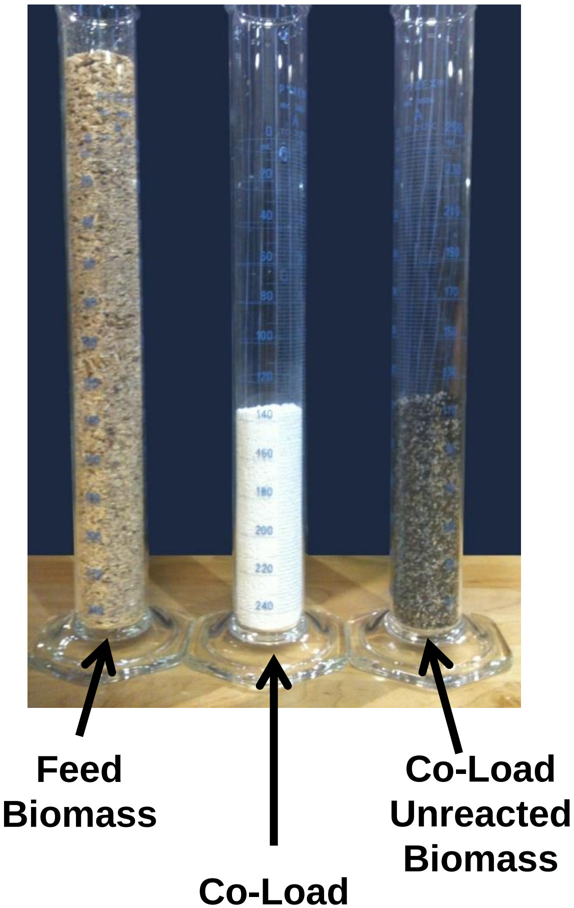
***Illustrative result shown based on literature results for conventional pyrolysis and hydrolysis.**

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

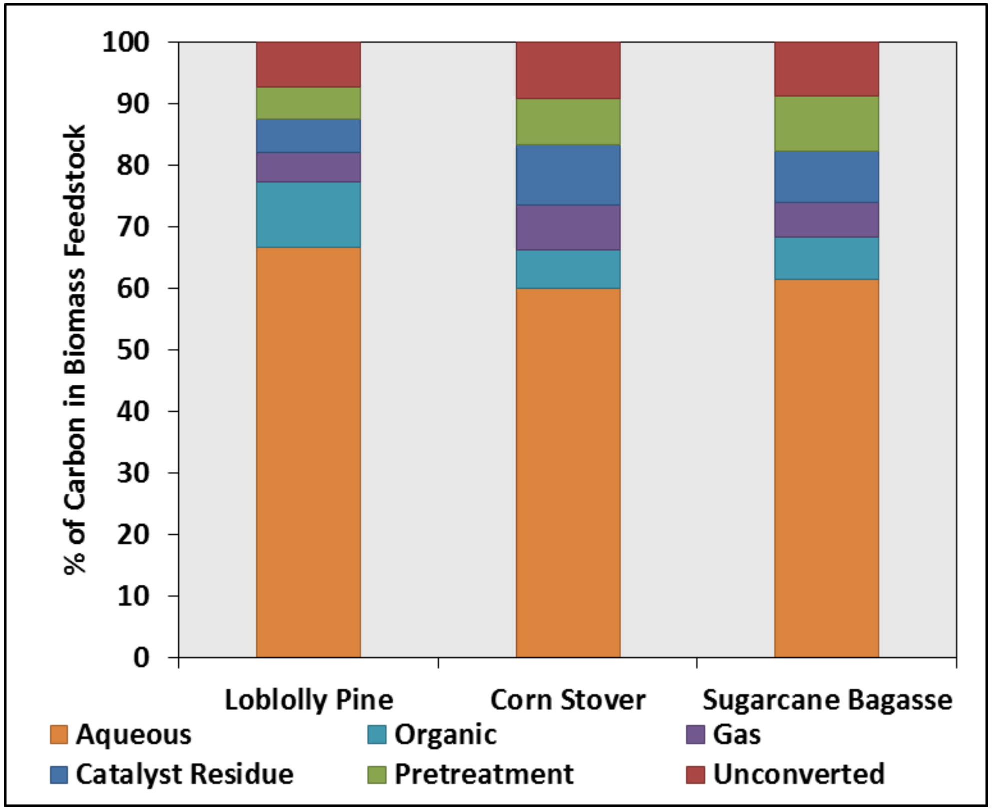
Biomass Solvolysis

- Large Reactor Loaded with Biomass and inert Co-Load Material



- Following Solvolysis all that remains is co-load with dark, non-structural carbonaceous material and inorganic ash which can be removed by an oxidative regeneration.

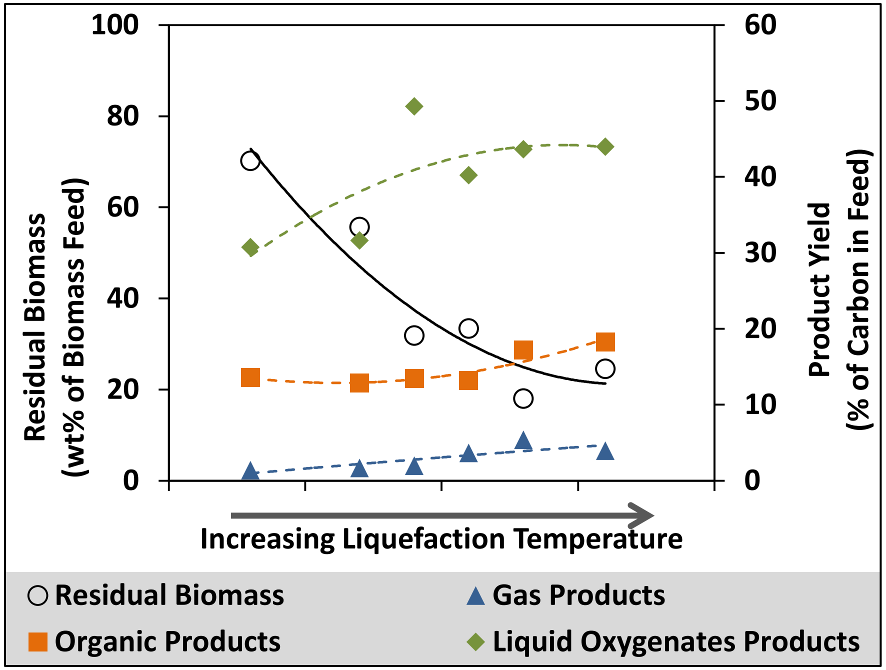
Biomass Species Effects on Solvolysis Product Profile

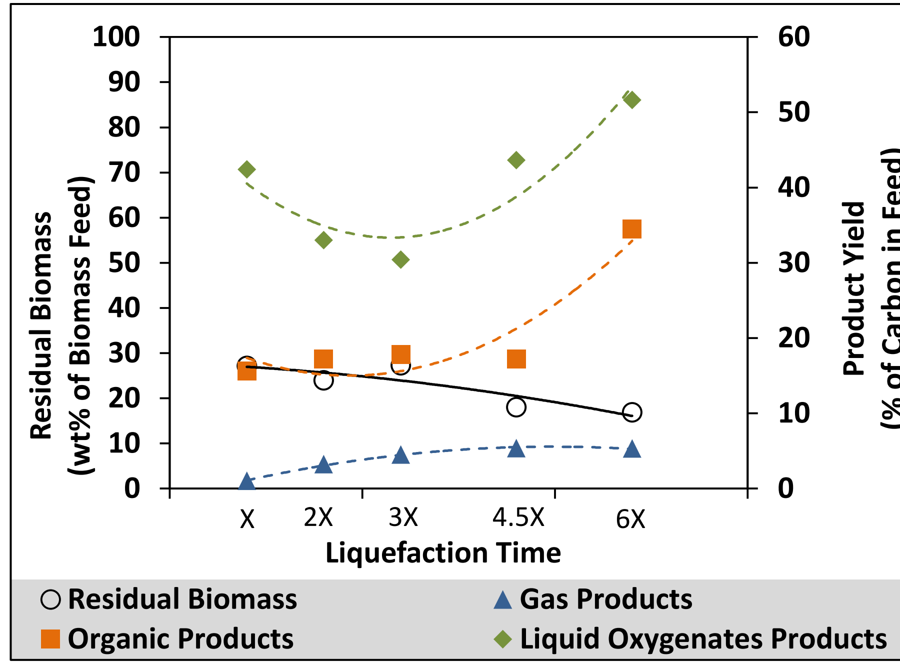


Biomasses composition and reactivity will affect the yield and selectivity to oxygenates at high biomass conversion.

The differences in solvolysis conversion and product suitability for condensation will guide the feedstock downselect.

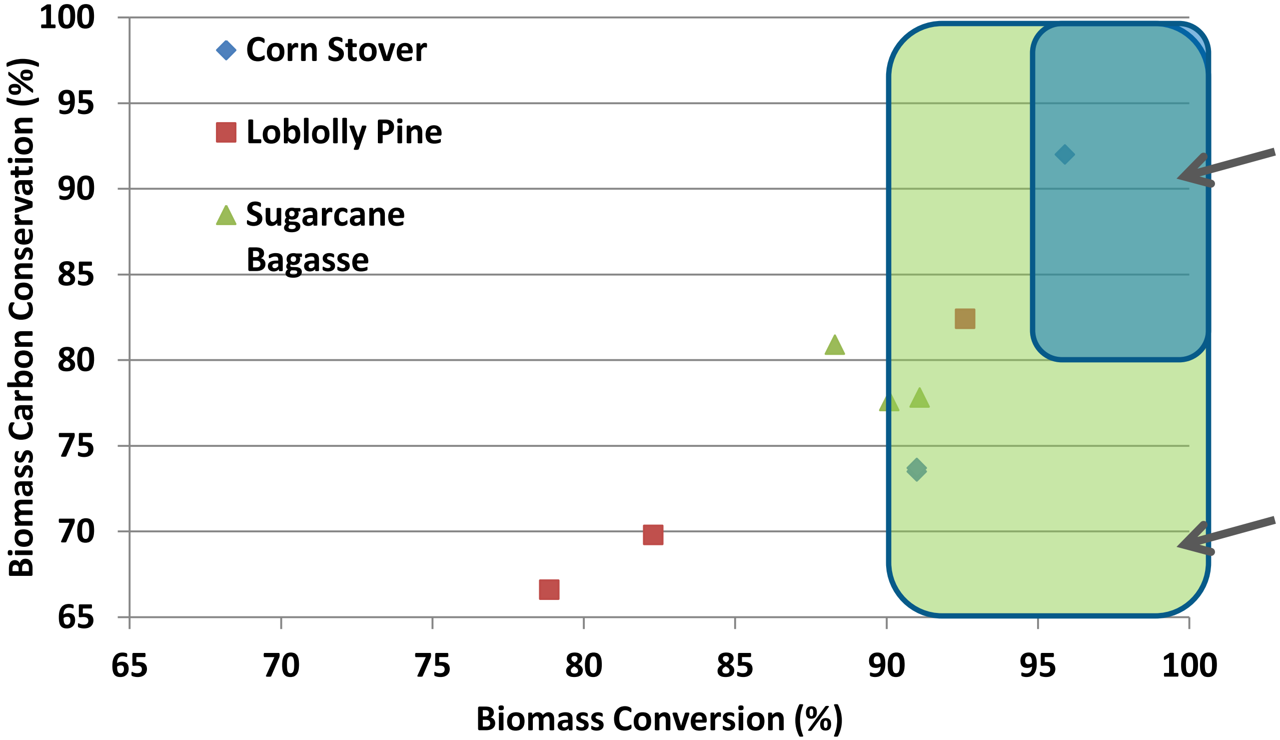
Solvolysis Condition Optimization





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

Solvolysis Conversion VS Conservation



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

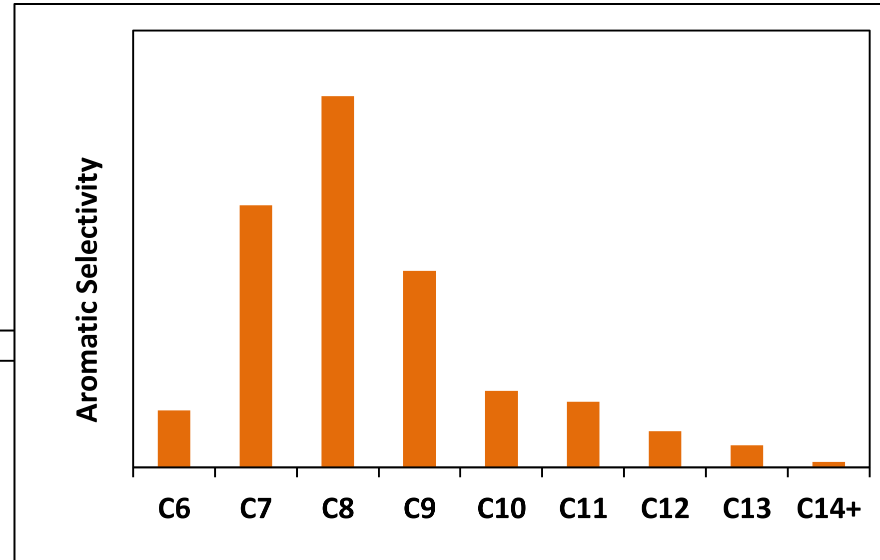
Completed Milestone
>90% Biomass Solubilization

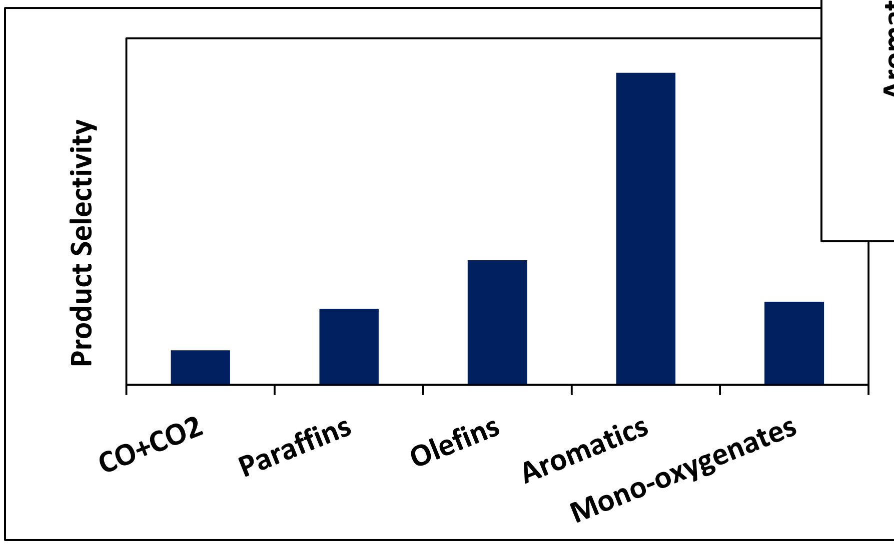
Biomass Conversion – weight % of liquefied biomass

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)

Condensation of Solvolysis Products

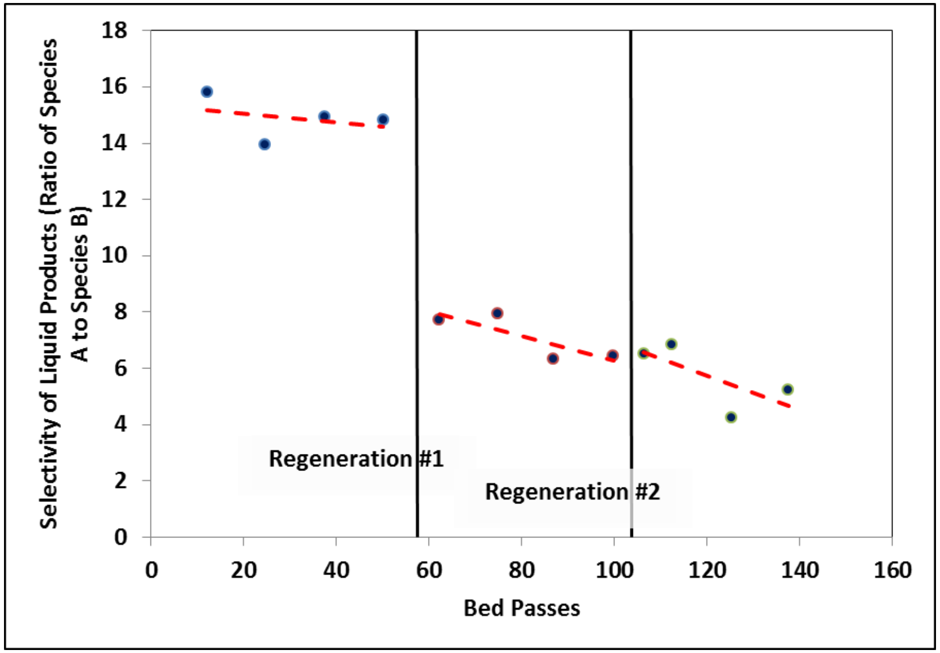
Initial investigations have shown high yields of an aromatic rich hydrocarbon product

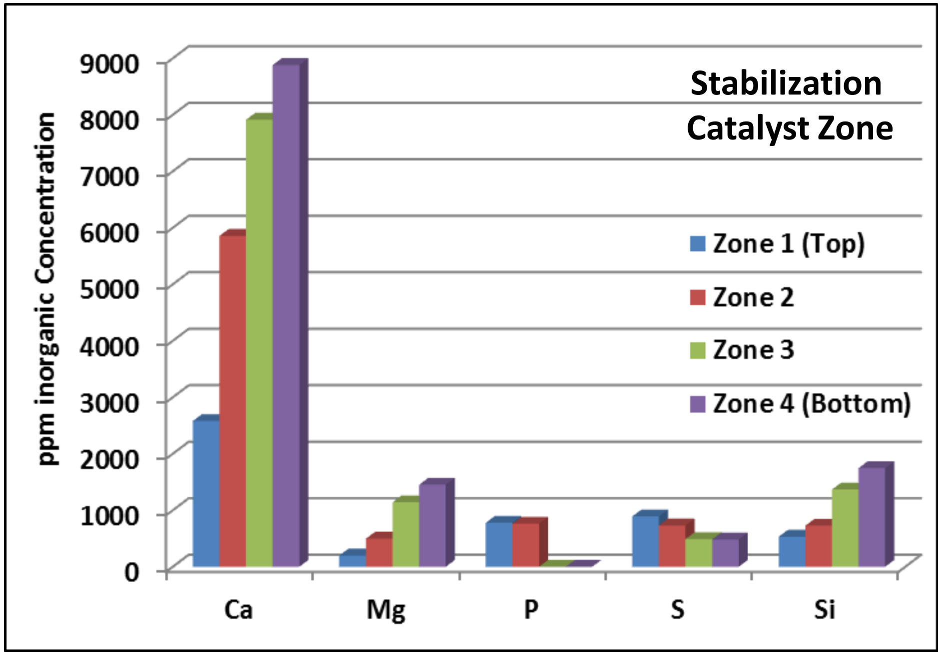




Condition and catalyst scoping and process optimization be leveraged to improve aromatics selectivity by 50% to maximize value in fuels and chemicals applications

Contaminant Effects on Stabilization Catalyst Stability

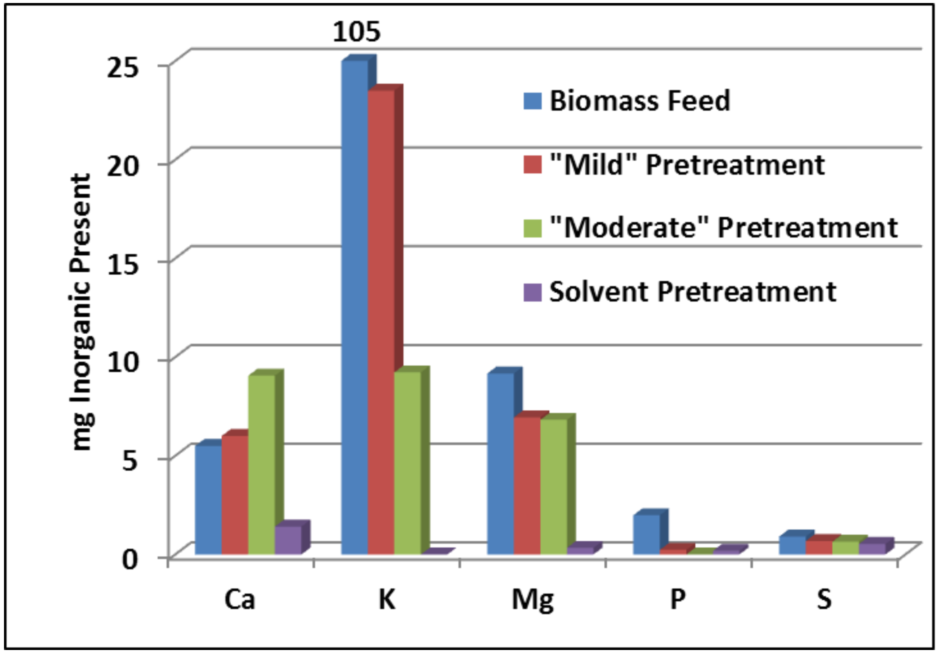


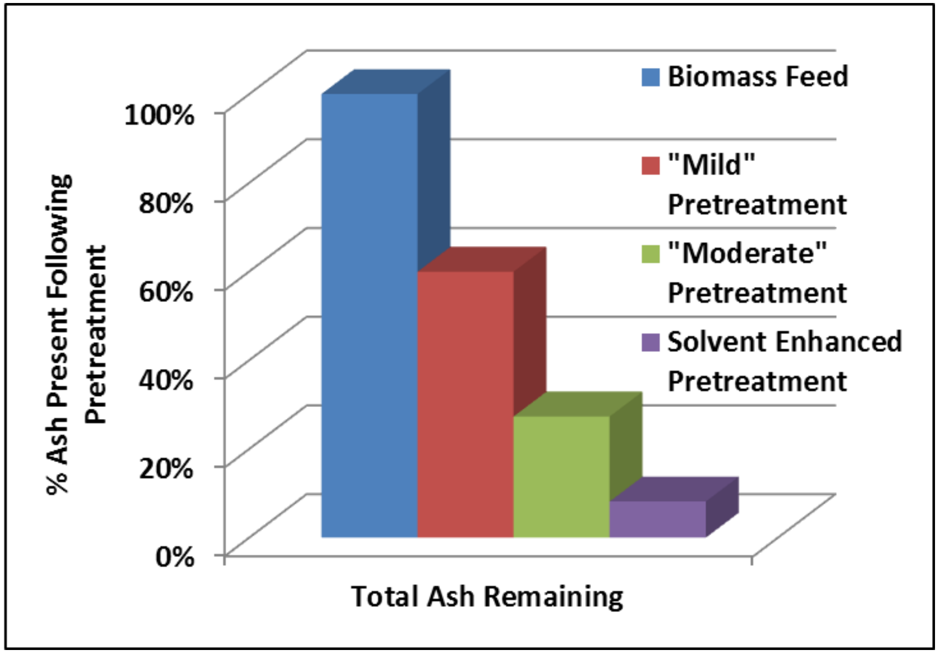


The stabilization catalyst shows substantial deactivation that cannot be recovered through typical catalyst regeneration procedures.

Post mortem catalyst analysis shows substantial deposition of biomass ash components on the catalyst surface.

Biomass Pretreatment to Reduce Contaminants





“Mild” Pretreatment allows for ~40% Ash Removal with <5% Carbon loss

“Moderate” Pretreatment allows for ~70% Ash Removal with ~20% Carbon loss

More severe and solvent enhanced washes are capable or removing >70% and >90% of the ash respectively but with an increased carbon loss during pretreatment

Achievements and 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
- Project Directives
  - – Downselect to a single feedstock with most promising deconstruction path to Aromatics
  - – 2000 hr run with theoretical catalyst lifetime of 1 yr
  - – Develop TEA model for deconstruction process

Relevance

Addresses Thermochemical Conversion R&D Strategic Goal:

- *"…develop commercially viable technologies for converting biomass feedstocks into energy dense, fungible liquid fuels, such as renewable gasoline, jet fuel, and diesel, bioproducts and chemical intermediates, and bioenergy."*

Addresses high-impact research areas in MYPP:

- Hydrothermally stable catalysis and/or processing of bio-oils
- Maximizing carbon utilization

Addresses the following BETO crosscutting goals:

- Single-pass stover is used as this is a necessary step for sustainable production
- Forest harvest residuals are used instead of stemwood

Critical Success Factors

- Reduced impact of biomass contaminants on system performance
  - Current work shows limited stability of the stabilization catalyst due to the contaminants in the biomass
  - Focus of future work on understanding effects of contaminants and develop improved performance by improved biomass pretreatment and contaminant tolerant stabilization catalyst.

- Prove the viability of a continuous deconstruction process
  - Preliminary work has all been conducted in batch or semi-batch modes, while successful commercial deployment requires continuous operation.
  - Focus of future work on design, construction, and operation of an continuous system that integrates the solvolysis and condensation technologies and use information from this integrated system for process scale up and TEA evaluation.

Future Work

- **Pretreatment** – Improve contaminant removal while conserving carbon. *Q2 2013*
- **Feedstock Downselect** – Determine most favorable feedstock for years 2 & 3 based on solvolysis yields and condensation evaluation. *Q2 2013*
- **Condensation** – Achieve a baseline performance and scope processing conditions to improve product yields and selectivities. *Q4 2013*
- **TEA** – Determine system cost and scale up cost; Sensitivity analysis to determine critical action items and tasks to improve economics. *Q3 2013*

Biomass

Pretreatment

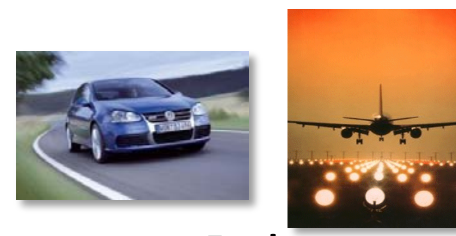
-Removal of:
*Ash/Inorganics
*"Extractives" in Biomass

Solvolysis

-Solubilize carbohydrates as well as lignin
-Stabilize to favorable Intermediates

Condensation

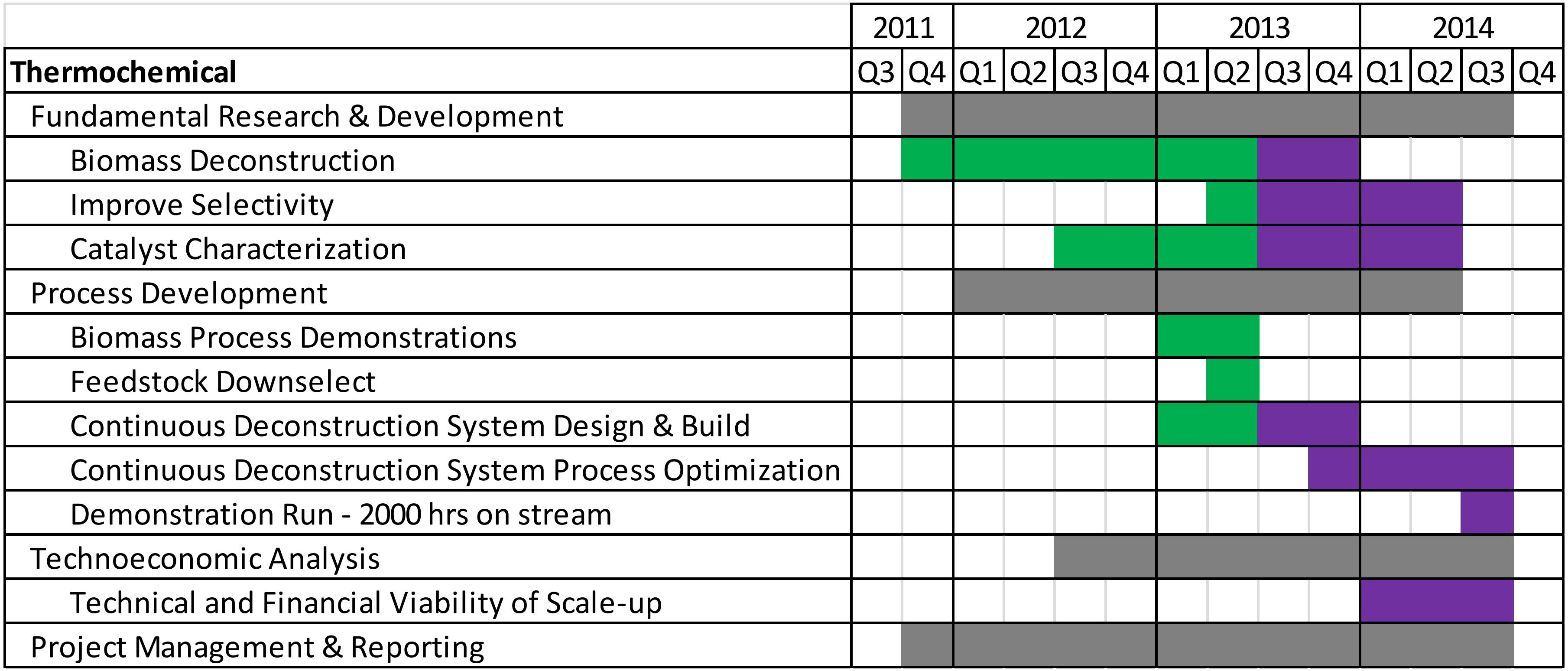
-Upgrading of solubilized biomass intermediates to Fuels and Chemicals



Fuels

Bio-Benzene and Chemicals

Future Work – Gantt Chart



Complete or In Process

Future Work

Summary

- Solvolysis
  - Utilizes unique solvents created by the stabilization process to liquefy lignocellulosic biomass
  - Capable of liquefying both carbohydrate and lignin fractions
- Process Development
  - >90% liquefaction has been achieved
  - >80% conservation of carbon intermediates for condensation to fuels and chemicals
  - Condensation produces an aromatic rich hydrocarbon product
- Future Focus
  - Aromatics yield improvement from solvolysis intermediates
  - Pretreatment for contaminant removal and catalyst lifetime improvement
  - Construction of a continuous deconstruction unit

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Additional Slides

Responses to Previous Reviewers' Comments

- This program was not reviewed in 2011

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Publications, Presentations, and Commercialization

- No update for this peer reivew

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