Cellulosic Biomass Sugars to Advantaged Jet Fuel

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Technology Area Review: Biochemical Conversion

Randy Cortright PhD
Virent, Inc

WBS: 2.3.1.8

VIRENT

Goal Statement

Project Goal – Integrate Virent's BioForming® Process with NREL's biomass deconstruction technology to efficiently produce cost effective "drop-in" fuels from corn stover with particular focus in maximizing jet fuel yields.

- **Improve pretreatment strategies** for deconstruction of cellulose and hemicellulose while significantly reducing or eliminating costly enzymes
- **Process intensification** through the potential elimination of enzymatic hydrolysis and/or catalytic processing steps
- **Improve yields** of jet fuel through utilizing "convertible carbon" intermediate streams (compounds previously considered "degradation products"), catalyst development and process optimization

Quad Chart Overview

Timeline

- Start: October 2011
- End: July 2014
- Percent complete: ~30%

Barriers

- Bt-D. Pretreatment Processing
- Bt-I: Cleanup/Separation
- Bt-J: Catalyst Development
- Bt-K. Biochemical Conversion Process Integration

Budget

Budget Period 1:($8.64 MM / $2.22MM)
Budget Period 2:($4.74 MM / $1.22MM)
Years the project has been funded: 1.5
Average annual funding: $4.46MM

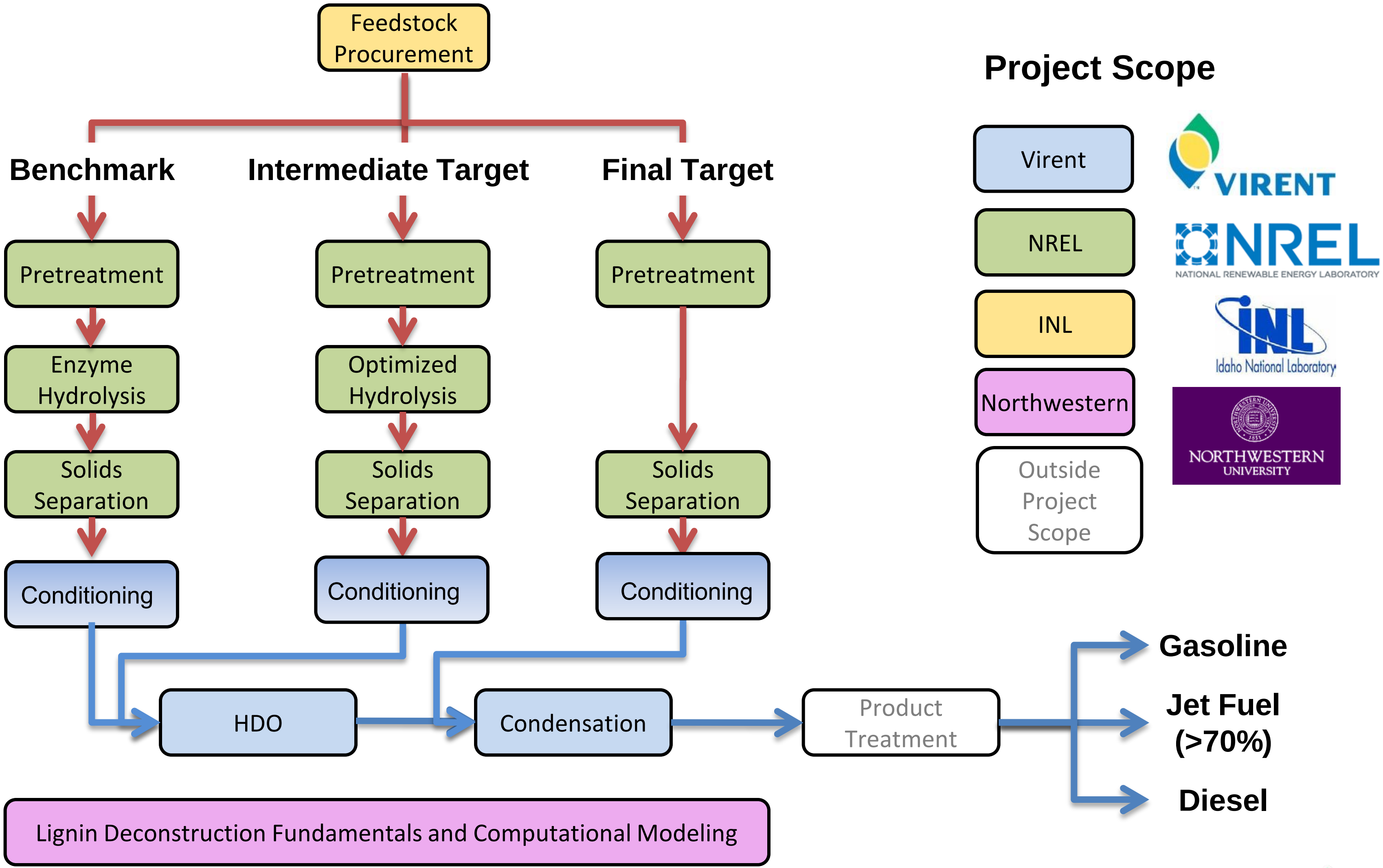
Partners

National Renewable Energy Lab (Deconstruction and Catalyst Characterization)
Idaho National Laboratory (Feedstock Supply)
Northwestern University (Lignin Fundamentals)

Project Overview

- The prime objective is to develop an integrated process that can efficiently and cost-effectively convert corn stover to a mix of hydrocarbons ideally suited for blending into jet fuel. Given that Virent's BioForming process can utilize a much wider range of oxygenated compounds than just monomeric sugars—enabling flexibility in pretreatment strategies—the following project objectives are targeted:
    - advancement of pretreatment strategies that deconstruct cellulose and hemicellulose while significantly reducing/eliminating costly enzyme use;
    - process simplification via potential elimination of enzymatic hydrolysis and/or catalytic processing steps; and
    - higher yields of "convertible carbon" intermediate streams using compounds that were once considered either "degradation products" or otherwise undesirable for subsequent conversion.

Technical Approach Summary



Feedstock Procurement

Benchmark

Pretreatment

Enzyme Hydrolysis

Solids Separation

Conditioning

Intermediate Target

Pretreatment

Optimized Hydrolysis

Solids Separation

Conditioning

Final Target

Pretreatment

Solids Separation

Conditioning

HDO

Condensation

Product Treatment

Gasoline

Jet Fuel (>70%)

Diesel

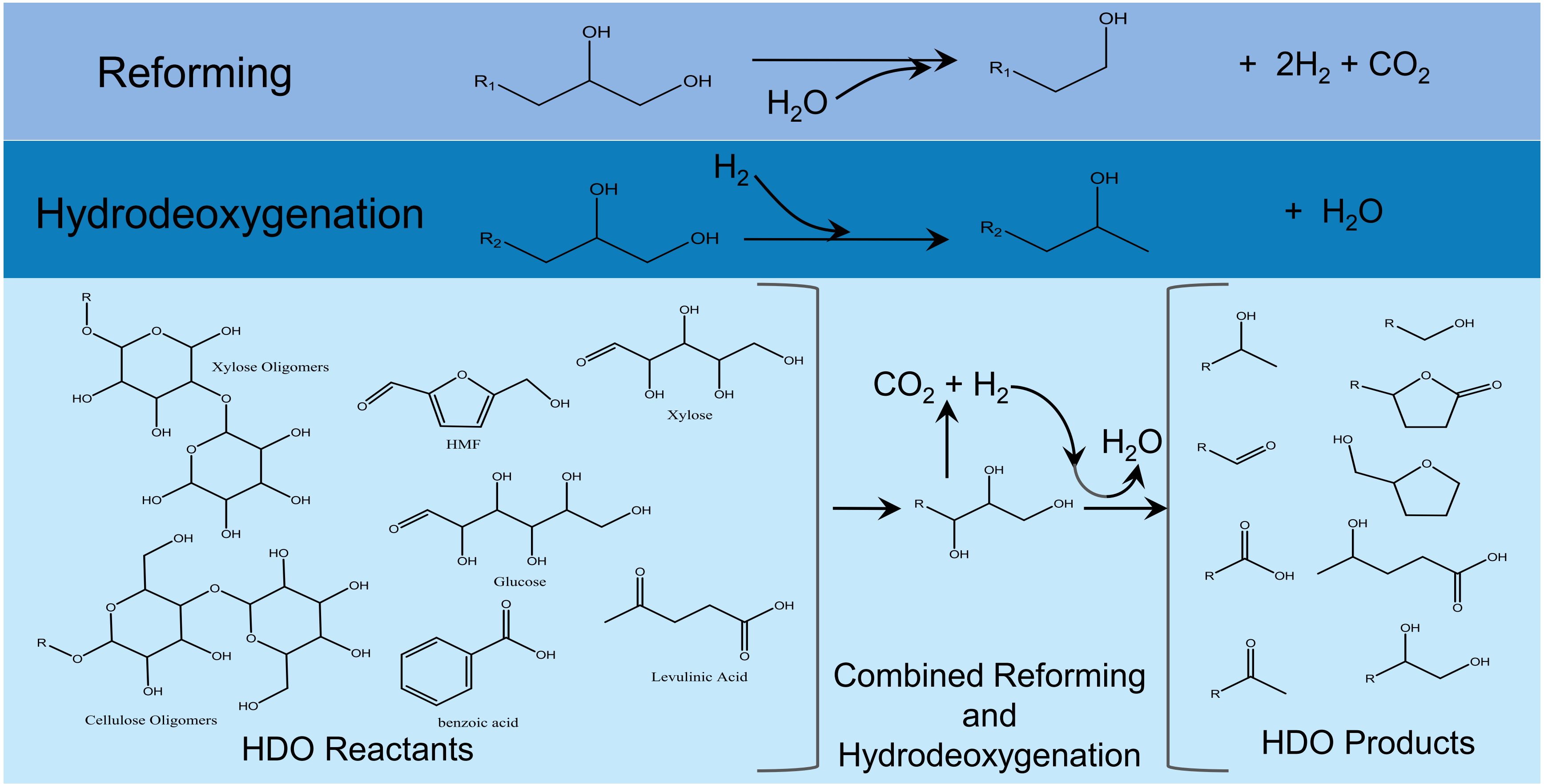
Lignin Deconstruction Fundamentals and Computational Modeling

Project Scope

- Virent
- NREL
- INL
- Northwestern
- Outside Project Scope

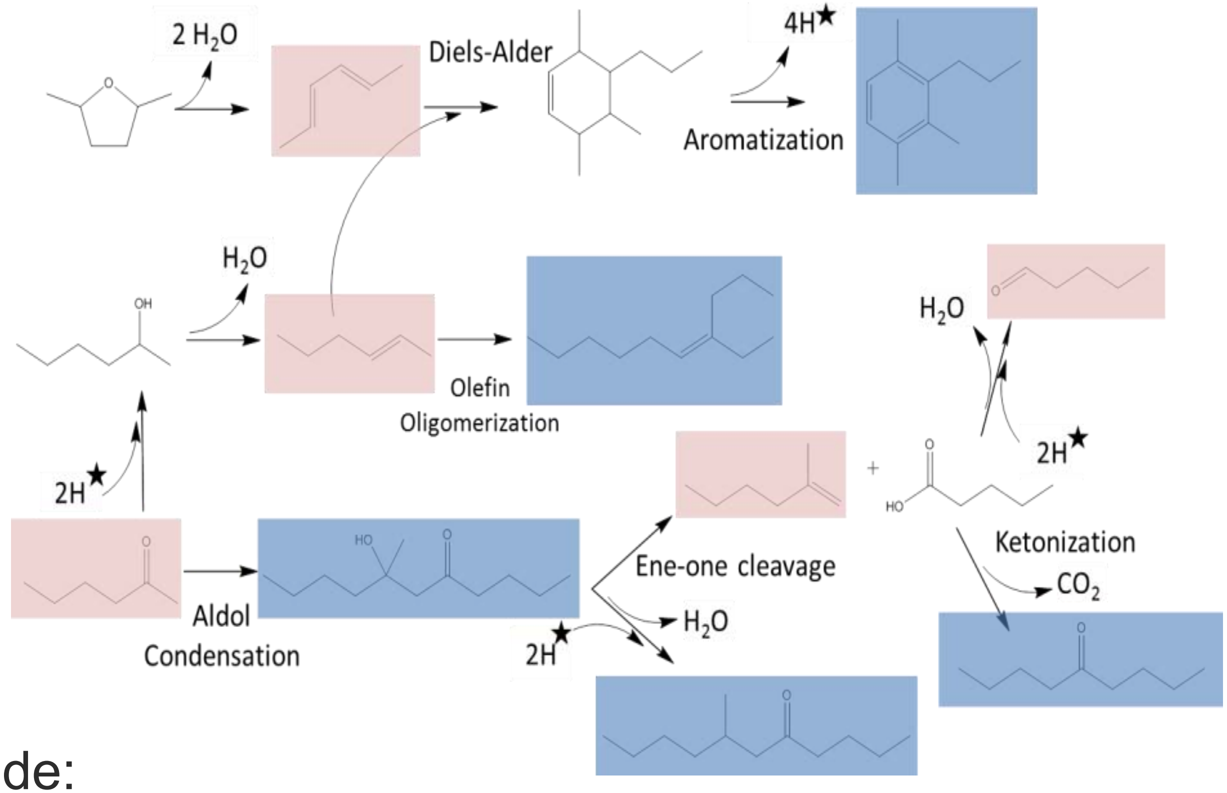
Technical Approach

HDO Reaction Pathways to Reactive Intermediates



- Intermediate oxygenate composition impacts downstream processing
- Intermediates can be tuned to achieve different final product goals

Distillate Condensation Chemistry



Pathways include:

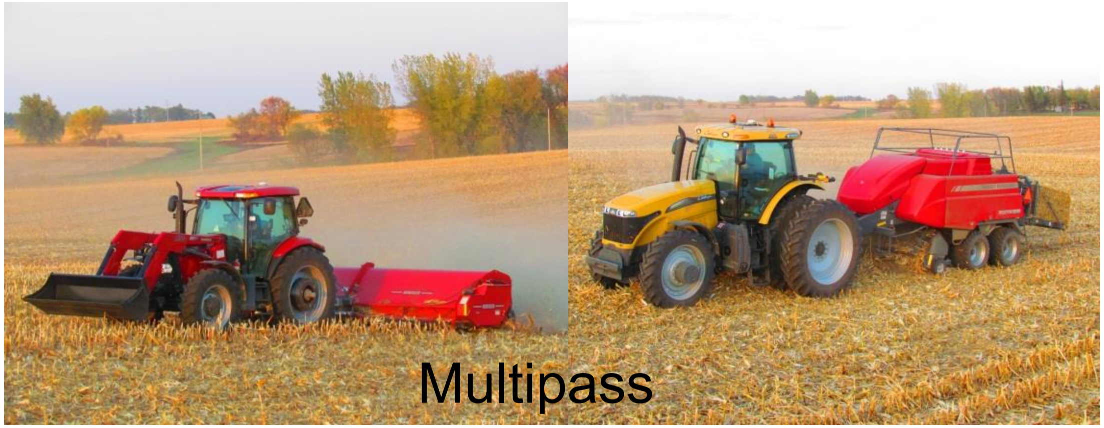
- Diels-Alder condensation of dienes and olefins,
- Oligomerization of olefins,
- Aldol condensation of carbonyls, and
- Ketonization reactions between organic acids to yield a ketone and carbon dioxide.

Note: Pink – Condensation reactants; Blue – products ready for hydrotreating

Feedstock – Corn stover supply

- ‘Consistent’ feedstock required for entire project (validation)
- Procured and stored >15 tons each of single pass and multipass corn stover.
- Indoor bale storage study initiated to monitor moisture and potential yield losses
- Supersacks of ground, dried single pass corn stover delivered to NREL on request (roughly four tons to date)
- Proximate and ultimate analyses, BTU (HHV and LHV), ash content, and ash composition measured for grab samples collected over the course of two grinds


Single pass


Multipass

Benchmark – Biomass Deconstruction

- Single-pass harvest corn stover, ¾ inch hammer milled (INL)

Acid Impregnation

High-Solids Continuous Pretreatment

High-Solids Enzymatic Hydrolysis

- Yields exceeded Benchmark Case targets

Deconstruction Product Yields

Glucose from Glucan	84%
Xylose from Xylan	80%
Soluble Carbon from Cellulose	93%
Soluble Carbon from Hemicellulose	98%

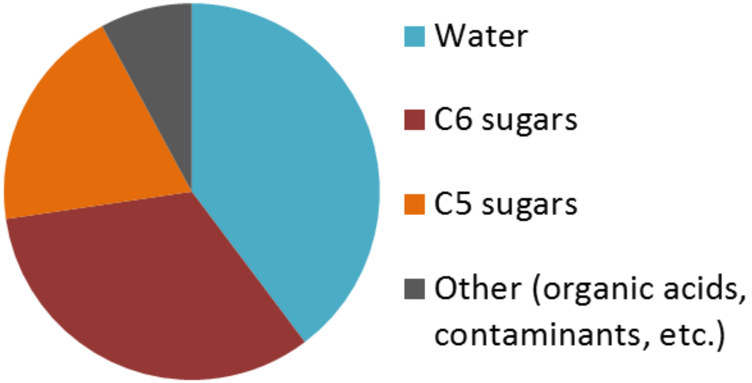
Benchmark – Hydrolysate Conditioning

- Residual solids removed by filtration
  - Lignin in biomass is not fully deconstructed
  - Particle size range: 0.2 micron up to 0.2 cm
- Solids will damage lab-scale pumps and plug packed-bed reactors
  - Remove solids by filtration

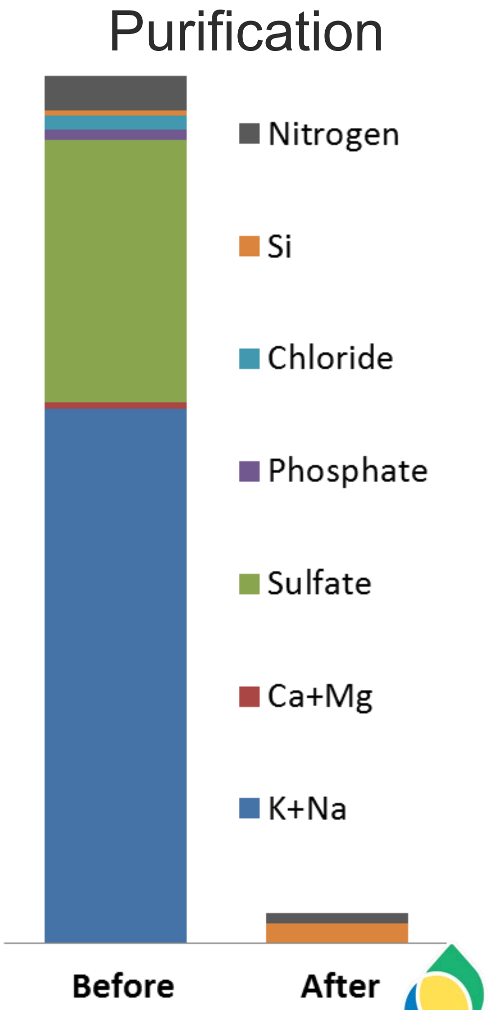
Left: Liquor product
Above: Unreacted solids
Right: Clarified liquid

Benchmark – Hydrolysate Conditioning

- Contaminants not amenable to catalytic processing
  - Biomass ash, process chemicals
  - Precipitation, catalyst poisoning
- Purify to remove contaminants
- Hydrolysate contained excess water
  - Utility demand, reaction kinetics
  - Concentrate to 40-60% sugars by evaporation

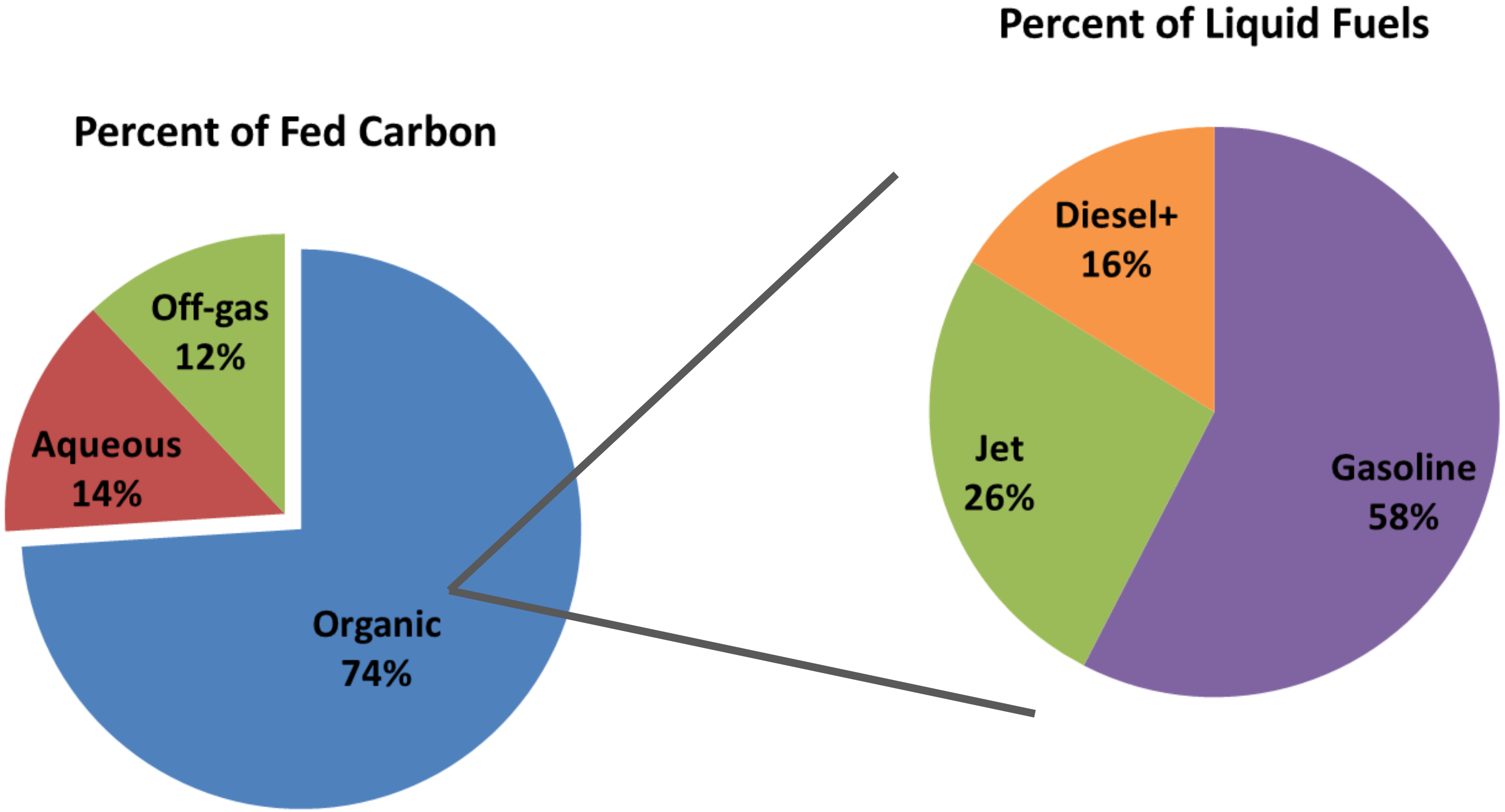


Carbon content of conditioned hydrolysate



Benchmark – Catalytic Conversion

- Purified corn stover hydrolysate fed to BioForming process.
- Process on stream for 10 days
- Overall Liquid Fuel Yield, 74%, gasoline was most abundant product



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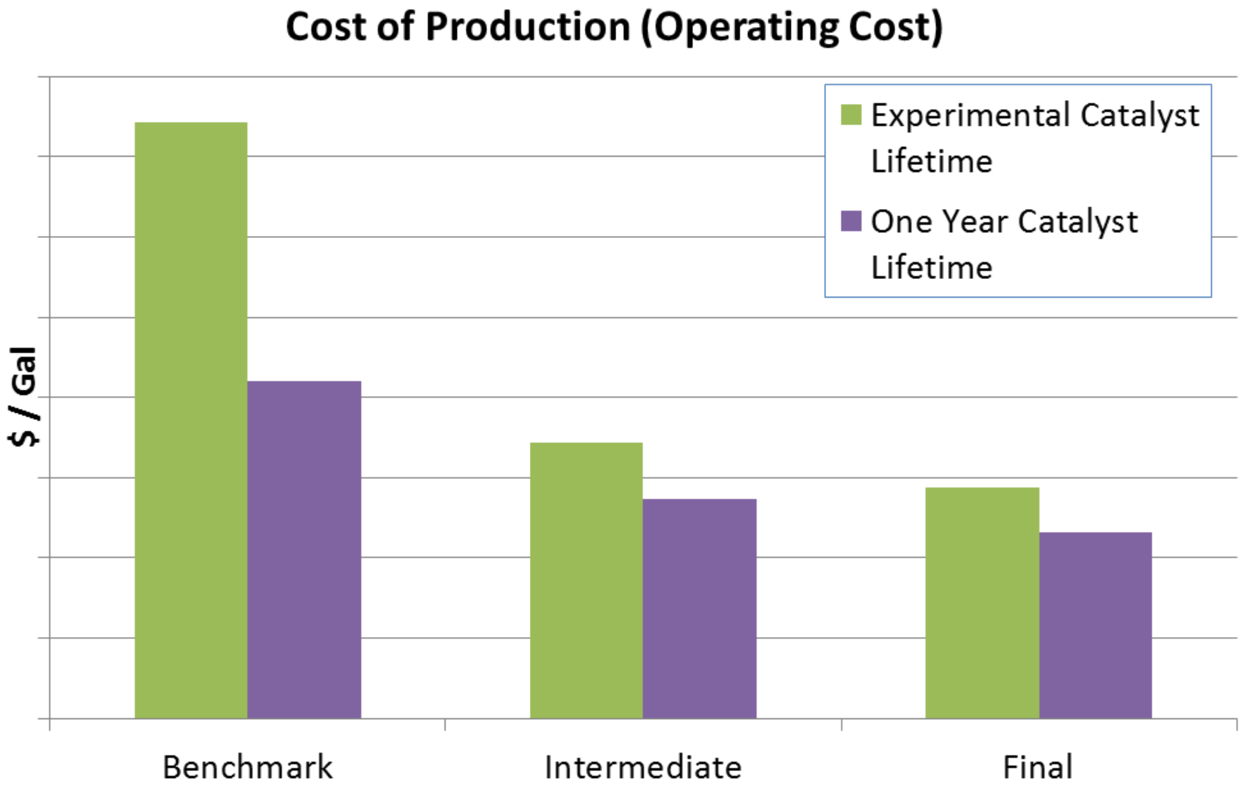
Benchmark – TEA

- TEA was a hybrid method
  - Yields, WHSV and product profile from validation run
  - Heat and material balances from corn syrup Aspen model
  - Experimentally proven lifetimes are from corn syrup feedstocks
- Working capital removed from the model



Benchmark Validation – Feedback

- Areas of Excellence
  - Well prepared and qualified project team
  - Compositional analysis capabilities
  - Facilities of adequate scope and scale to meet project demands

Area for Improvement	Improvement approach (in progress or completed)
Improve jet fuel selectivity	Catalyst and process development for improved jet fuel selectivity
Validate or eliminate normalization assumptions in data analysis	Commenced review of normalization assumptions
Improve documentation and clarity on yield calculations and data flow	Documented calculations and data flow
Increase fidelity of TEA analysis	Developed workplan to address this and all validation team concerns

Intermediate Investigations

- Biomass Deconstruction
  - Minimize catalyst contaminates in the hydrolysate
  - Reduce enzyme utilization
  - Lignin fundamental kinetic studies
- Hydrolysate Conditioning
  - Optimize solid-liquid separations
  - Investigate alternate purification techniques
- BioForming of Hydrolysates
  - Catalyst development
  - Model compound studies
- System Development
  - Improve carbon utilization
  - Process intensification

Biomass Deconstruction

- Larger scale operation
- Two stage pretreatment to achieve partial cellulose hydrolysis
  - Lower enzyme usage to convert remaining insoluble carbohydrates

Impregnation Screw Press

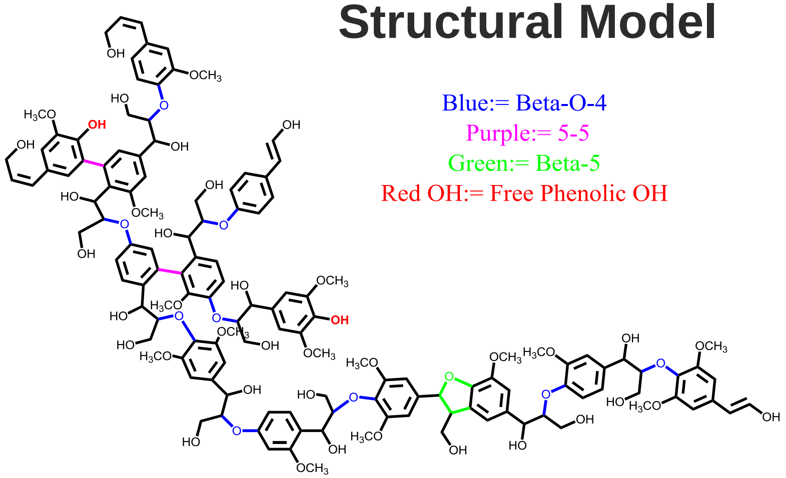
Pretreatment Reactor

Enzymatic Hydrolysis Reactor

- Process development in progress
- Intermediate Case deconstruction validation planned for Q4 2013

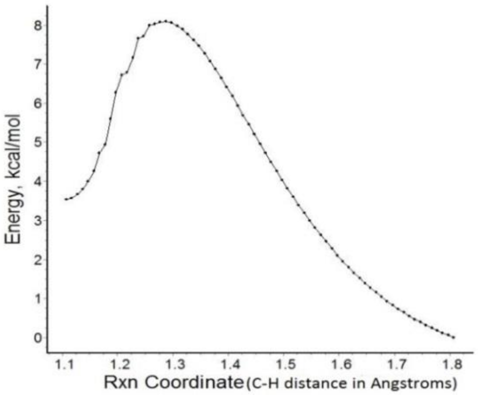
Lignin Deconstruction – Fundamental Understanding for Improved Carbon Recovery

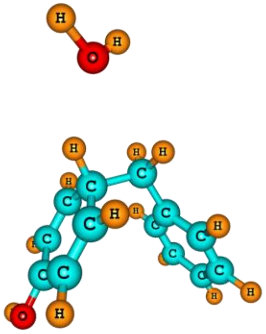
Structural Model



Representative Wheat Straw Lignin Molecule

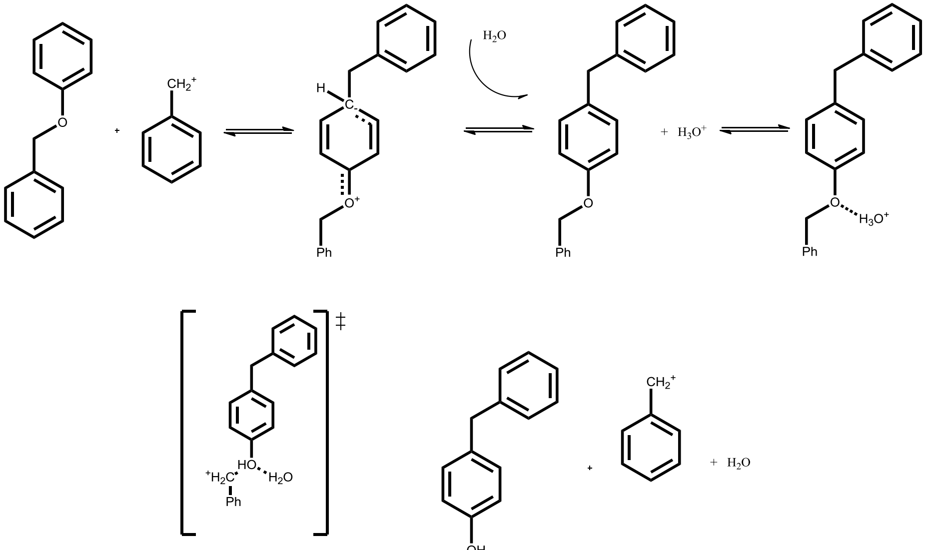
Electronic Structure Calculations





Barrier Height of H-Abstraction

Using Kinetic Monte Carlo, Apply Microkinetic Model to Library of Lignin Structures to Obtain Detailed Product Distribution



Stochastic Chemical Simulation Method

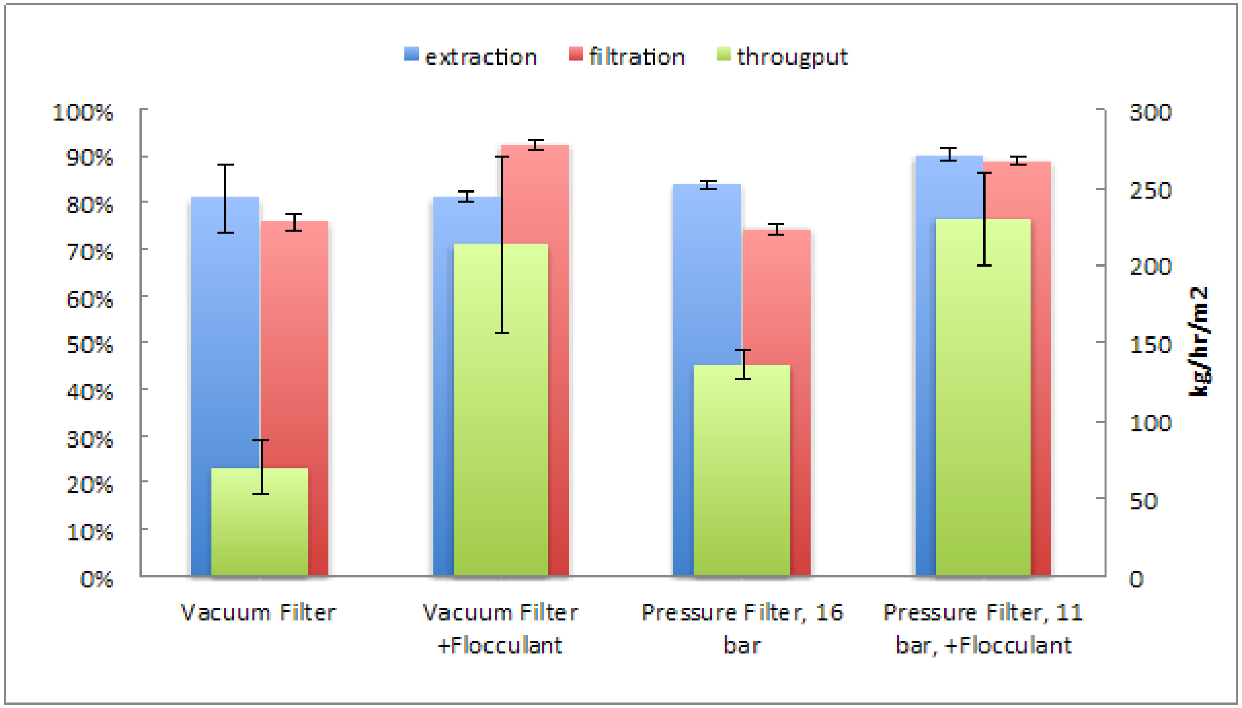
With $r_1, r_2 \in [0,1]$, select:

$$\tau = \frac{1}{a_0(\mathbf{x})}\log\left(\frac{1}{r_1}\right) \qquad \mu \quad \text{s.t.} \quad \sum_{i=1}^{\mu} a_i > r_2 a_0(\mathbf{x})$$

where a_i is rate of elementary step i

Hydrolysate Conditioning

- Utilizing filtering basket centrifuge for hydrolysate solid-liquid separations
- Conducting solid-liquid separation studies to improve separability and soluble carbon recovery, including impact of flocculants

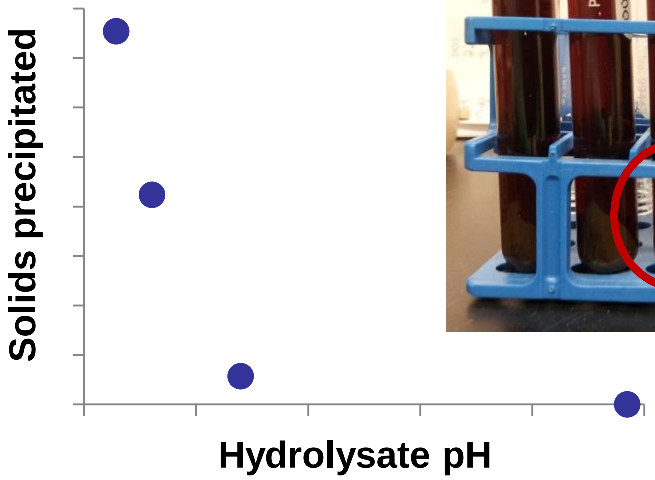


Filtering Basket Centrifuge

Hydrolysate Conditioning

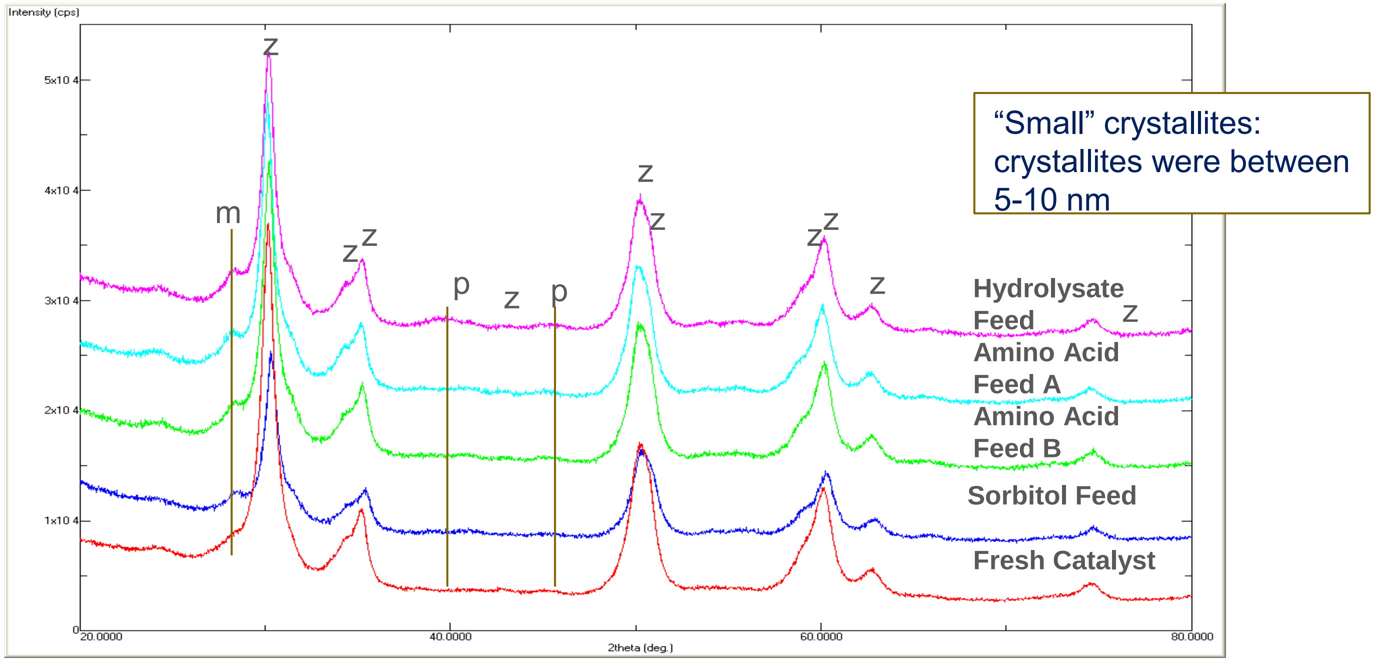
- Identifying key carbon losses during conditioning
  - Change in pH causes precipitation during purification
    - Alternative process configurations, purification methods under development to improve carbon recovery
  - Volatile losses in evaporation
    - Process conditions scoping, azeotropes may limit improvements

Process	***Benchmark Yield***	***Target yield***
Filtration	100%	-
Purification	92%	
Evaporation	94%	-
Overall	86%	91%



Fundamental Work

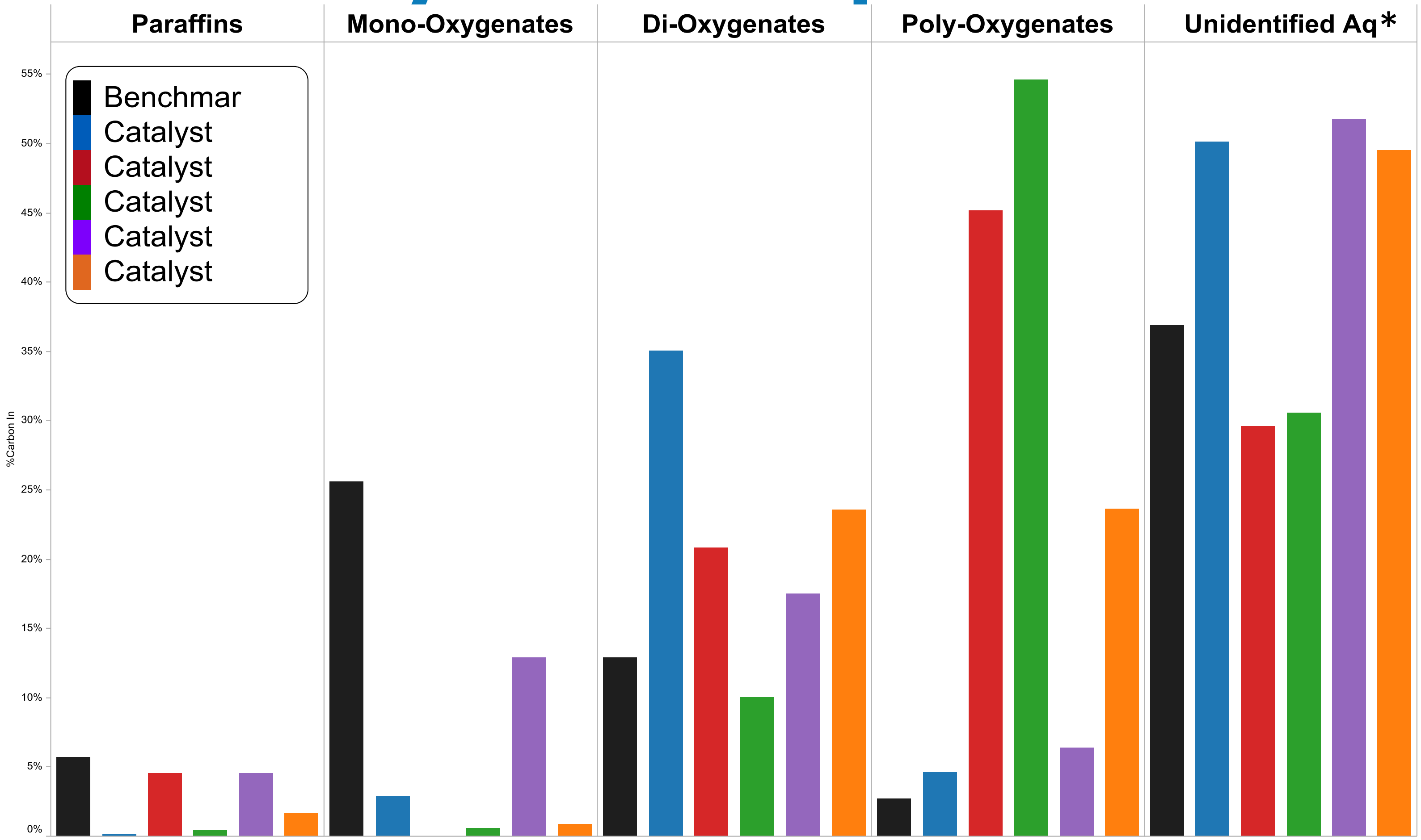
HDO Catalyst Characterization



“Small” crystallites: crystallites were between 5-10 nm

- Surface poisoning of catalysts
  - Evaluation of systems with model components and real hydrolysates
- Crystallite size changes
  - Active metal sintering
  - Support structural changes
- Carbon density of deposits on catalyst surface

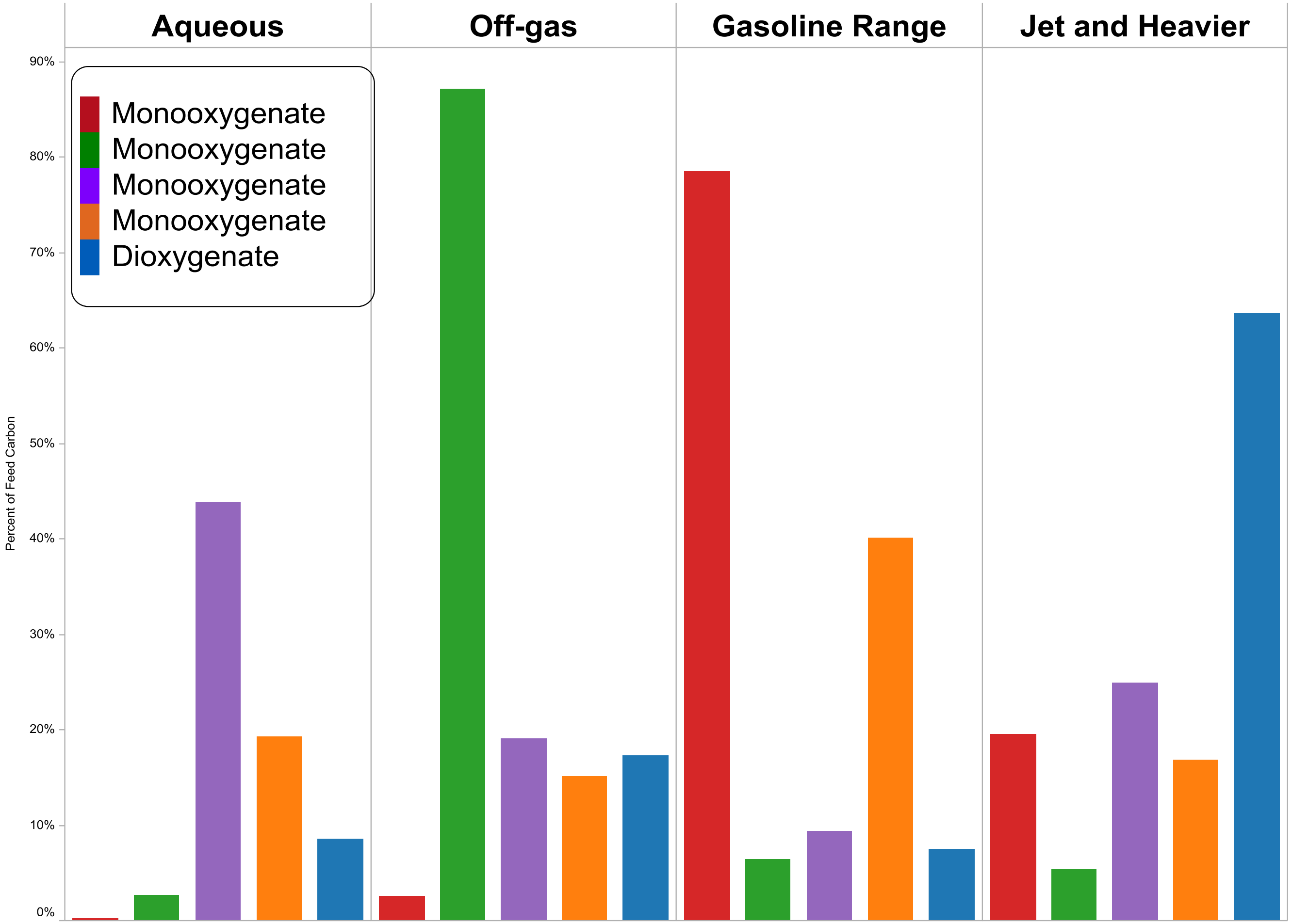
HDO Catalyst Development



*Unidentified Aq are water soluble partially-deoxygenated sugar species

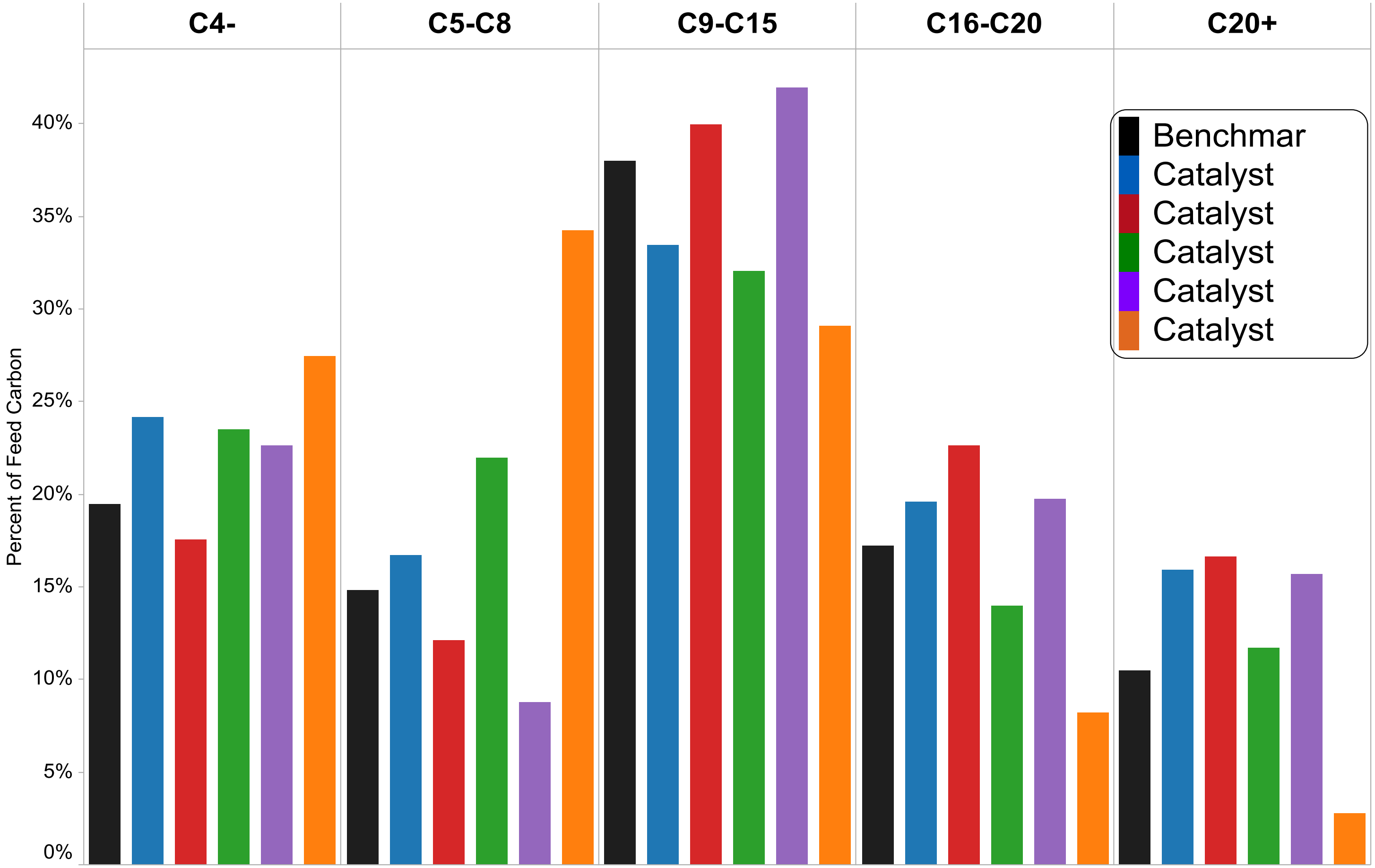
- Non-precious metal based catalysts were evaluated to lower cost and provide increased contaminant resistance
- 70+ catalyst formulations screened
- Selectivity can be tuned from poly-oxygenates to paraffins with catalyst formulation

Condensation Studies with Model Compounds



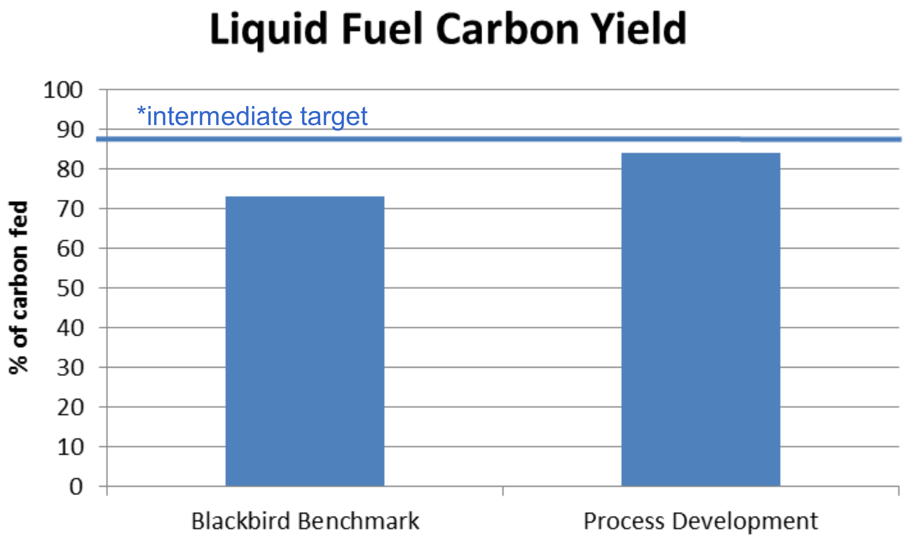
- Several representative HDO product components evaluated to determine optimal HDO product liquid distillate fuel yields.
- Dioxygenated species improves distillate yield and preferred HDO product.

Condensation Catalyst Development



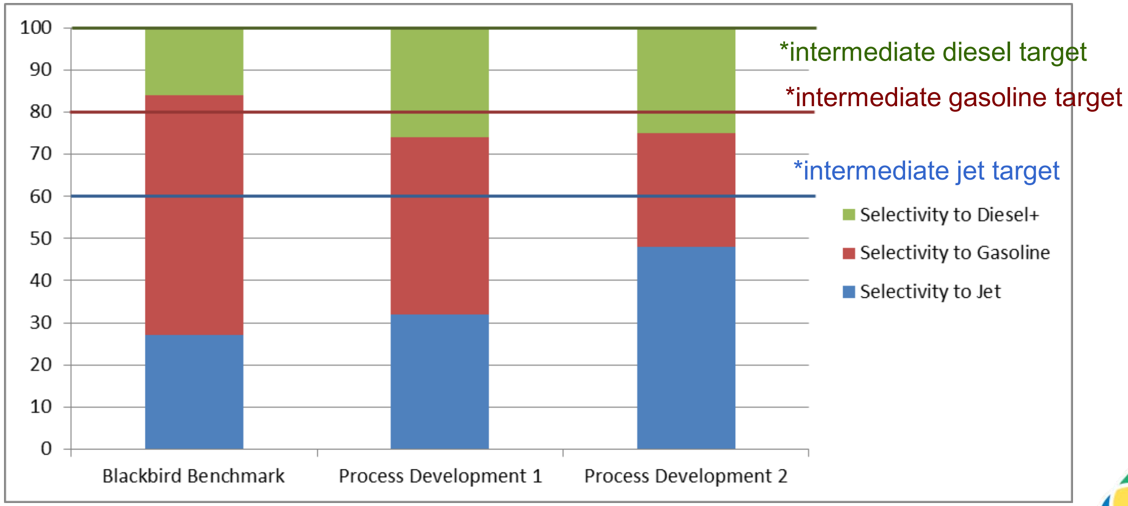
- Low cost supports and metals were tested to improve TEA
- 15+ catalysts screened
- Several catalysts were more selective to Jet Range, C9-C15.

Combined Process Optimization



Liquid fuel carbon yield improved by 10%

Selectivity to Jet improved by greater than 20%

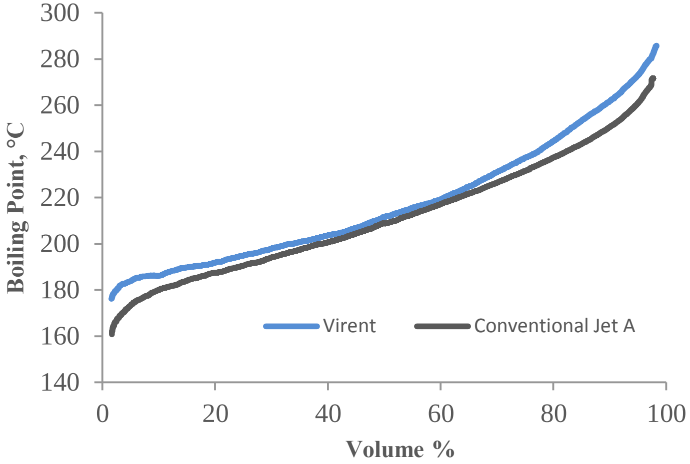


Fully Synthetic Renewable Jet Fuel

Specification Test	MIL-DTL-83133G Spec Requirement	JP-8	VIRENT
Physical and Chemical Properties			
Heat of Combustion (measured), MJ/Kg	≥42.8	43.3	43.3
Flash point, °C	≥38	51	40
Freeze Point, °C	≤-47	-50	<-60
Density @ 15°C, kg/L	0.775 - 0.840	0.804	0.805
Distillation			
10% recovered (T_{10}), °C	≤205	182	164
EP, °C	≤300	265	290
T_{90}-T_{10}, °C	≥22	62	86
Thermal Stability			
Temperature		260°C	325°C
Tube Deposit Rating	<3	1	1
Change in Pressure, mm Hg	≤25	2	0

Excellent freeze point and density due to unique Virent jet composition

Virent D-86 comparison to Jet-A



High thermal stability ensures low levels of impurities

Achievements and Milestones

- **Biomass Deconstruction**
  - ✓ Completed benchmark of deconstruction and solid-liquid separation
  - ✓ Lowered total enzyme usage
  - Eliminate enzyme utilization (Q2 2014)
- **Hydrolysate Conditioning**
  - ✓ Completed benchmark of hydrolysate conditioning
  - Maximize carbon recovery and reduce conditioning costs (Q3 2013)
- **BioForming of Hydrolysates**
  - ✓ Completed benchmark BioForming process
  - ✓ Lowered HDO and Condensation catalyst cost through development
  - ✓ Improved BioForming yields and selectivity to jet fuel
  - Complete initial catalyst poisoning and deactivation studies (Q3 2013)
  - Eliminate HDO reaction step (Q2 2014)
- **Project Directives**
  - ✓ Completed benchmark techno-economic analysis
  - Complete Intermediate TEA and financial viability of scale-up (Q4 2013)
  - Complete Intermediate Validation and Stage Gate Review (Q4 2013)

Relevance

- Addresses Biochemical Conversion R&D Strategic Goal: *"To develop commercially viable technologies for converting biomass feedstocks into energy dense, fungible liquid transportation fuels…"*

This Project addresses three high-impact research areas in MYPP

- Lower pretreatment costs
- Lower enzyme costs (or eliminate)
- Developing catalytic conversion routes for <u>advanced biofuels</u>

This work further addresses crosscutting goals of BETO

Single-pass stover is used as this is a necessary step for sustainable production

Chemical Preconversion work in process

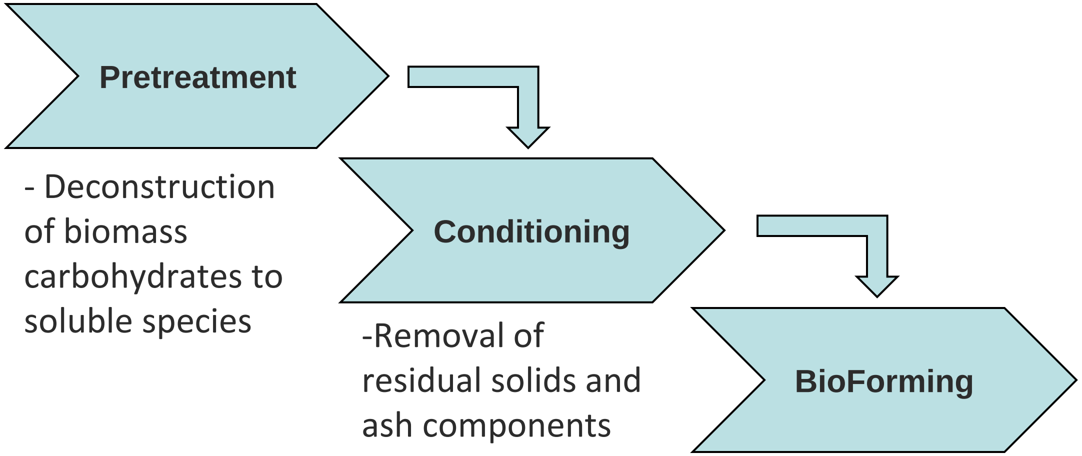
Critical Success Factors

- **Biomass Deconstruction** – Develop a process to maximize carbon recovery with a scalable process to soluble products well suited for catalytic upgrading
  - Historic work focused on monomeric sugar recovery
  - Future work to focus on wider range of deconstruction materials amenable to the BioForming process including oligomeric sugars and sugar degradation products
- **Hydrolysate Conditioning** – Reduction of the economic impact for the hydrolysate conditioning process
  - Historic work has shown losses of soluble carbon and high processing costs to
  - Future work to focus on increasing the contaminate tolerance of the BioForming catalysts to reduce purification burden and alternative hydrolysate conditioning schemes to maximize soluble carbon recovery
- **Combined Process** – Reduction in capital and operating costs of the biomass to jet fuel process.
  - Historic work has focused on integration of state of technology for the deconstruction, hydrolysate conditioning and BioForming processes without leveraging process synergies
  - Future work to focus on process intensification reducing the capital and operating costs of the program and yield/selectivity improvements for biomass deconstruction and the BioForming process

Future Work

- **Biomass Deconstruction** – Further reduce enzyme and chemical inputs. *Q3 2013*
- **Hydrolysate Conditioning** – Improve carbon recovery. *Q3 2013*
- **BioForming of Hydrolysates** – Continue to improve liquid fuel yield and jet fuel selectivity. *Q3 2013*
- **TEA** – Update process economics and capital cost estimates with intermediate stage improvements. *Q4 2013*
- **Intermediate Validation and Stage Gate Review** – Complete review of intermediate validation targets and go/no go decision by DOE. Q4 2013

Biomass



Pretreatment

- Deconstruction of biomass carbohydrates to soluble species

Conditioning

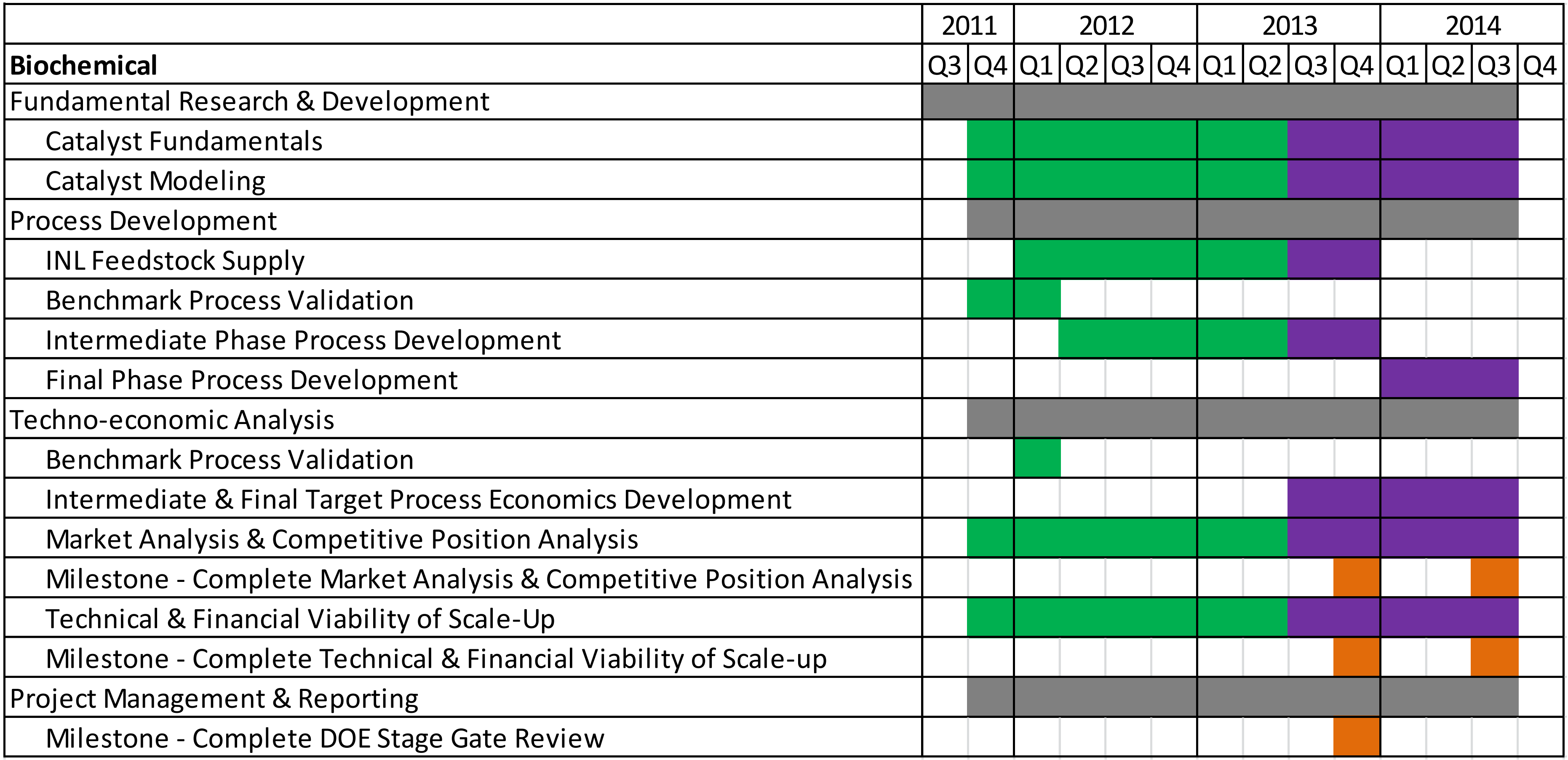
-Removal of residual solids and ash components
-Hydrolysate concentration

BioForming

-Upgrading to liquid fuels

Fuels

Future Work - Gantt



	2011		2012				2013				2014			
Biochemical	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Fundamental Research & Development	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	
Catalyst Fundamentals		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟪	🟪	🟪	🟪	🟪	
Catalyst Modeling		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟪	🟪	🟪	🟪	🟪	
Process Development		⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	
INL Feedstock Supply			🟩	🟩	🟩	🟩	🟩	🟩	🟪	🟪				
Benchmark Process Validation		🟩	🟩											
Intermediate Phase Process Development				🟩	🟩	🟩	🟩	🟩	🟪	🟪				
Final Phase Process Development											🟪	🟪	🟪	
Techno-economic Analysis		⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	
Benchmark Process Validation			🟩											
Intermediate & Final Target Process Economics Development									🟪	🟪	🟪	🟪	🟪	
Market Analysis & Competitive Position Analysis		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟪	🟪	🟪	🟪	🟪	
Milestone - Complete Market Analysis & Competitive Position Analysis										🟧			🟧	
Technical & Financial Viability of Scale-Up		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟪	🟪	🟪	🟪	🟪	
Milestone - Complete Technical & Financial Viability of Scale-up										🟧			🟧	
Project Management & Reporting		⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	
Milestone - Complete DOE Stage Gate Review										🟧				

🟩 Complete or In Process Task or Milestone

🟪 Future Task Efforts

🟧 Future Milestone

Project Summary

- BioForming Process
  - Feedstock flexible process for the production of liquid fuels
- Process and TEA Improvements
  - Reduction in enzyme usage
  - Improved liquid fuels yield and jet fuel selectivity
  - Lowered catalyst cost
  - Further improvements required to meet intermediate targets
- Fungible BioFuels
  - Virent jet fuel meets preliminary testing for JP8 and military specs at high blend levels

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Jonathan Stickel
David Thompson
David Templeton
Ryan Wilkinson
Liz Woods
Abraham Yanez-McKay
Matt Yung

NREL and Virent Analytical and Operations Teams

QUESTIONS?

Additional Slides

Responses to Previous Reviewers' Comments

- This program was not reviewed in 2011

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Publications, Presentations, and Commercialization

- There is no update for this peer review

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