Cellulosic Biomass Sugars to Advantaged Jet Fuel

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Technology Area Review: Biochemical Conversion

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VIRENT

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Goal Statement

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

- **Developing commercially Viable Bioenergy Technology**
  - **Improve pretreatment**
  - **Improve yields**
- **Reduction of Greenhouse Gas Emission**
  - **Non-Food Feedstock** – Corn Stover
  - **Improve yields**
- **Process Generates "Direct Replacement" Hydrocarbons compatible with today's transportation infrastructure**
  - **Distillate Range Products**
  - **"Advantaged" Jet Fuel**
- **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 2011
- Project End: April 2015
- Percent complete: ~95%

Barriers

- Bt-D: Pretreatment Processing and Selectivity
- Bt-H: Cleanup/Separation
- Bt-I: Catalyst Efficiency
- Bt-J: Biochemical Conversion Process Integration

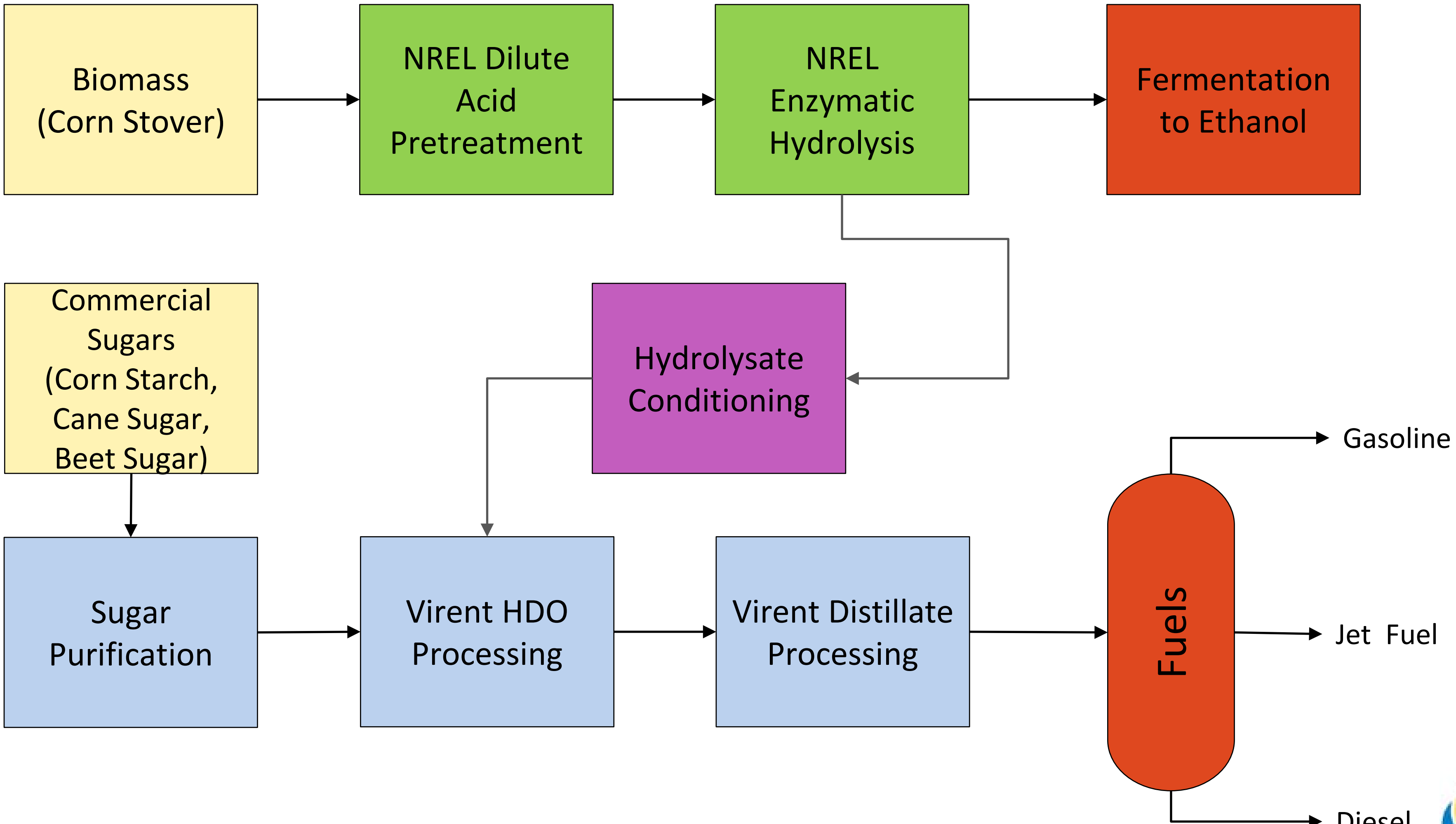
Budget

	FY10 –FY12 Costs	FY13 Costs	FY14 Costs	FY15-End Costs
DOE Funded	$1,302,899	$1,302,899	$2,683,382	$939,028
Virent Cost Share	$481,894	$481,894	$992,484	$347,312

Partners

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

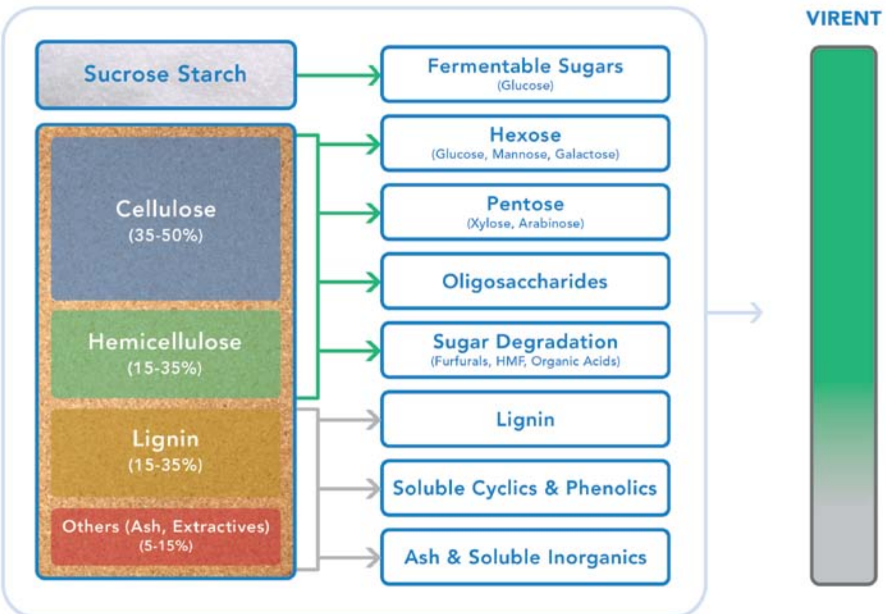
2 – Approach (Technical)



2 – Approach (Technical)

- **Overall Technical Approach**
  - **Combines** Virent's Catalytic Chemical Conversion Technology with NREL's Pretreatment and Enzymatic Deconstruction Technology
  - **Feedstock** - Corn Stover
  - **Products** - Distillate Range Hydrocarbons with a focus on Jet Fuel
- **Critical Success Factors**
  - **Ash Removal**
    - Necessary to Reduce Potential Catalyst Poisons
    - Partial Removal during Pretreatment followed by Final Clean-up through Hydrolysate Conditionings
  - **Carbon Recovery**
    - Maximize carbon recovery from hemicellulose and cellulose
    - Partial solubilization and conversion of lignin components
    - Maximize carbon conversion in the catalytic conversion to desired liquid hydrocarbon with improved selectivity to jet fuel.
  - **Product Certification** - ASTM and OEM approval/acceptance of biomass-derived Jet Fuel
  - **Process Economics** – Reduction in capital and operating cost of biomass to jet fuel process
- **Potential Challenges**
  - **Reduction** of Enzyme Cost
  - **Economical** methods of ash removal
  - **Improve** catalyst costs and lifetimes

2 – Approach (Technical)
Critical Success – Carbon Recovery



Greater Biomass Utilization

- BioForming® technology can handle a broad range of oxygenates derived from hemi-cellulose/cellulose fraction
  - C5 and C6 Sugars
  - Organic Acids
  - HMF
  - Furfurals

- Improved carbon yields from biomass as BioForming® technology is capable of converting solubilized lignin components.

- Primary concern is inorganic ash affecting catalyst lifetime and stability

Critical Success Factor – Jet Fuel Product Quality

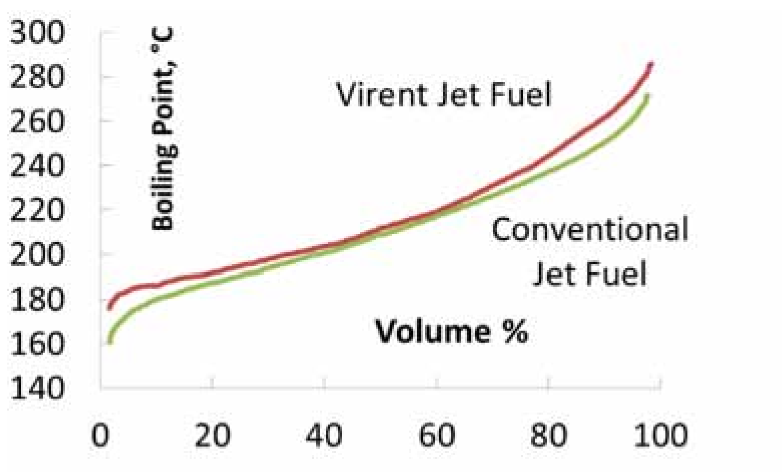
Meets all specifications up to 50/50 blend, advantaged relative to petroleum and other renewables

	ASTM D1655	Virent HDO-SK	Petro Jet*
Freeze Point	<-47°C	<-80	-44
Density	775-840 kg/m^3	812	806
Thermal Stability Breakpoint	>260°C	>355°C	285°C**
Sulfur	<0.3 wt%	<0.01	0.08**
T50-T10	15°C	35	34

*Commercial sample analyzed for comparison purposes

**Typical

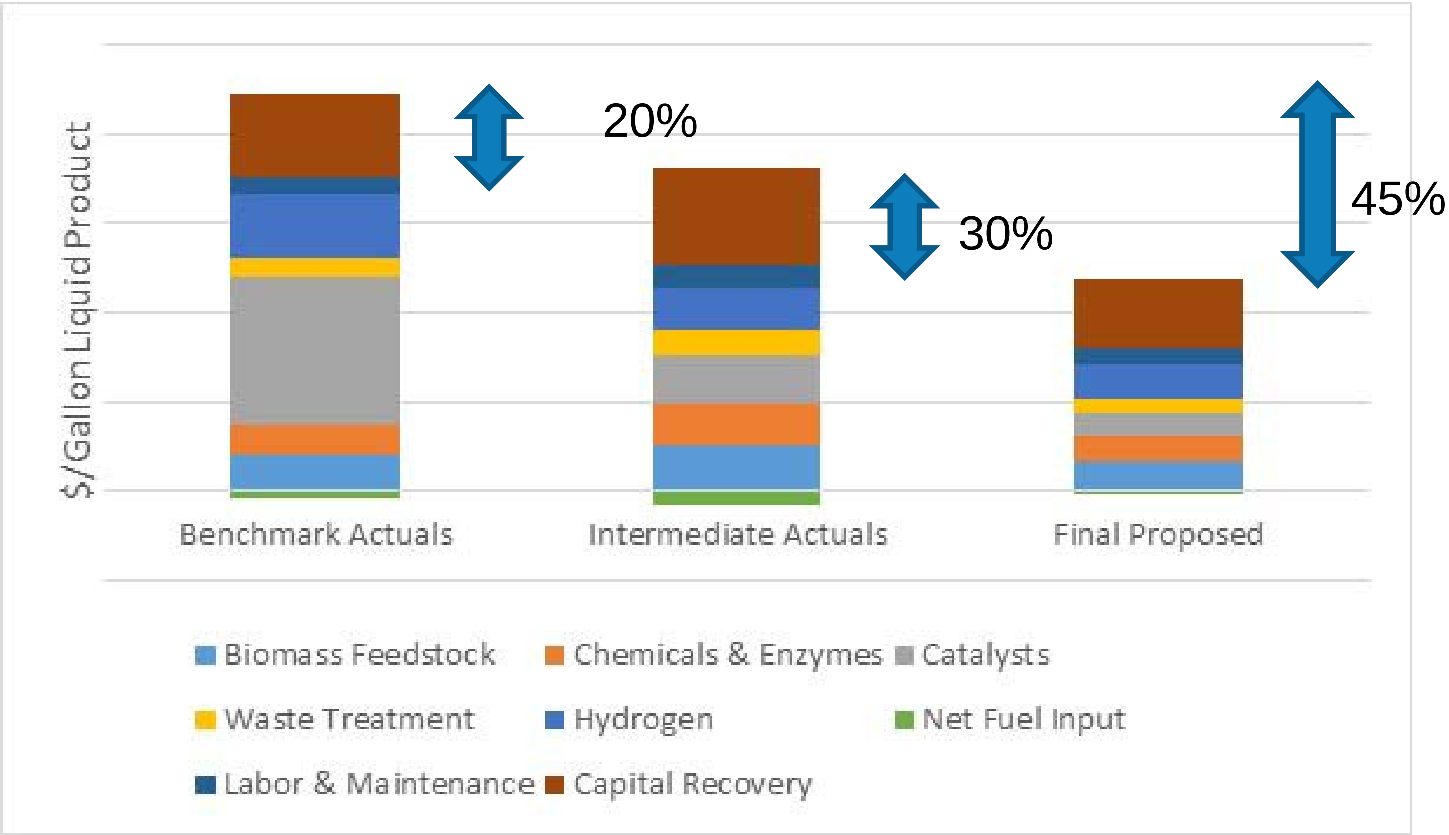
Broad distillation profile, consistent composition with different feedstocks



2 – Approach (Management)

- 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
  - Biomass Cost, Crude Oil Prices, Financing of Plant, Government Policy
- Management approach
  - Gantt Chart for 3 year project
  - Key Milestones
    - Benchmark Validation (March 2012)
    - Benchmark, Intermediate Validation (January 2014)
    - Benchmark, Final Validation (April 2015)
  - Stage Gate Review (February, 2014)
    - Re-scoping of Project
      - Decreased Focus on Deconstruction Technology
      - Increased Focus on Catalysis Improvements

Approach (Management)
(TEA of Overall Process)



- Improved Overall Cost of Liquid Product via improved catalyst performance.
- Expected further improvement through better yields, lower capital cost, and better catalyst performance.

3 – Technical Accomplishments/ Progress/Results

- **TEA -** Reduction in capital and operating cost of biomass to jet fuel process
- **Feedstock -** Economic collection and delivery of non-food biomass to a plant-gate using single-pass baling of stover
- **Biomass Pretreatment for Ash Removal -** Necessary to reduce potential catalyst poisons
- **Biomass Deconstruction –** Maximize carbon recovery with a scalable process to soluble products (including lignin components) well suited for catalytic upgrading
- **Hydrolysate Conditioning** - Necessary removal of potential catalyst poisons from soluble products
- **Catalytic Conversion –** Improved carbon yields and reduced catalyst cost.

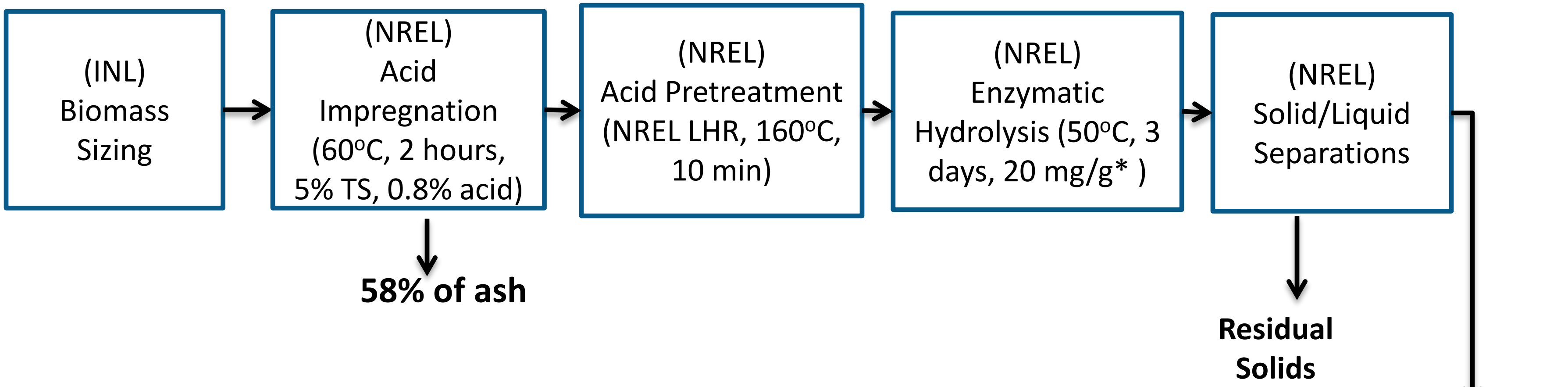
Ash Control in the Field

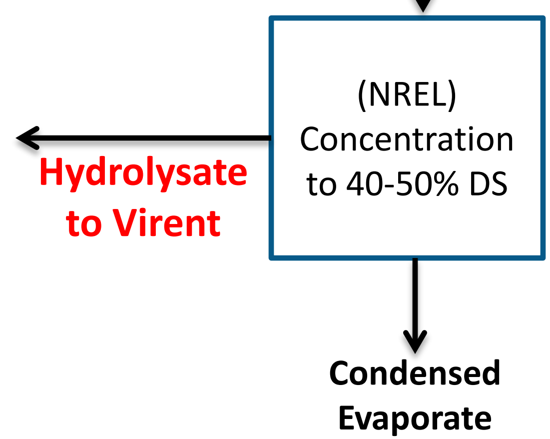
- Traditional stover collection is a multi-pass process – mowing followed by bailing
- New technology allows for single pass bailing of stover, reducing non-structural ash in the biomass
- INL procured and stored multiple tons of single pass and multi-pass corn stover.
- Completed a paper study of methods to reduce ash prior to arrival at the plant gate

Multipass

Single pass

Deconstruction – Final Case

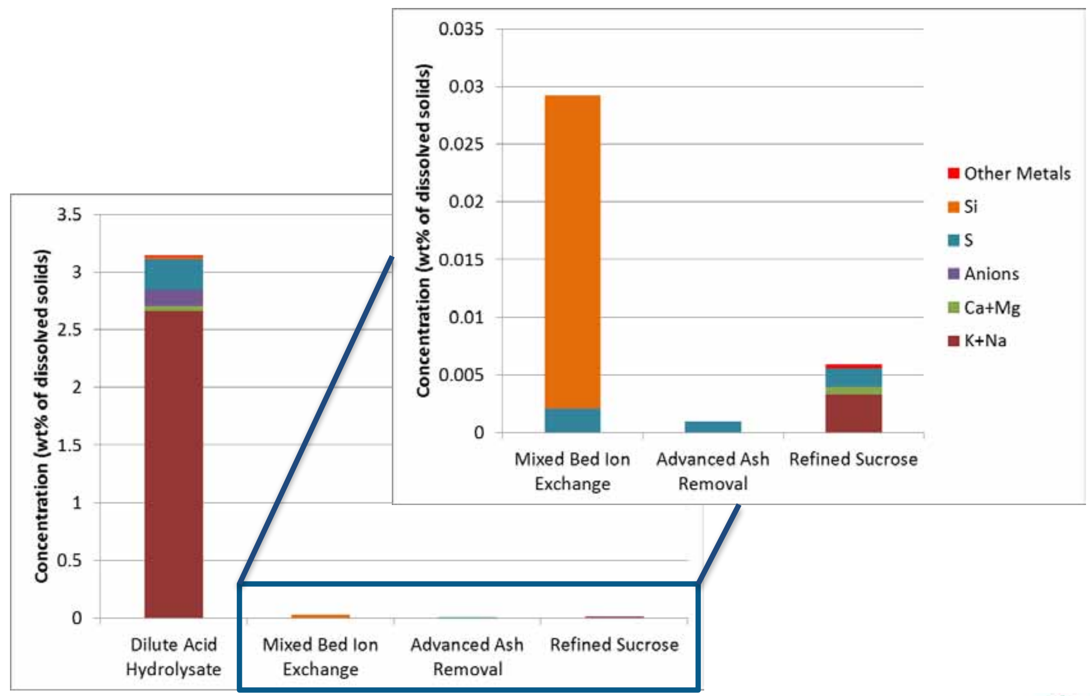




- Lower acid-impregnation solids loading to wash out more feedstock ash
- Reduction in ash content through lower acid loading and resulting neutralization
- Vacuum evaporation to produced concentrated hydrolysate
- Larger-scale equipment and batch sizes
    - 1000 kg concentrated hydrolysate batch

Hydrolysate Conditioning

- Transition from ethanol fermentation to catalytic processing required significant development to meet the size and purity specs for fixed bed systems
- Advanced purification technologies reduced the economic impact of purification while maintaining hydrolysate purity in alignment with conventional sugars



Catalytic Conversion Improvements

- Improved Carbon Recovery to Hydrocarbon Products
  - Changes in process line-up and process conditions

- Catalyst Improvements
  - Generation I Catalyst Support
    - Support used for both HDO and DHOG steps
    - Material is hydrothermally stable
    - Material is expensive and difficult to manufacture

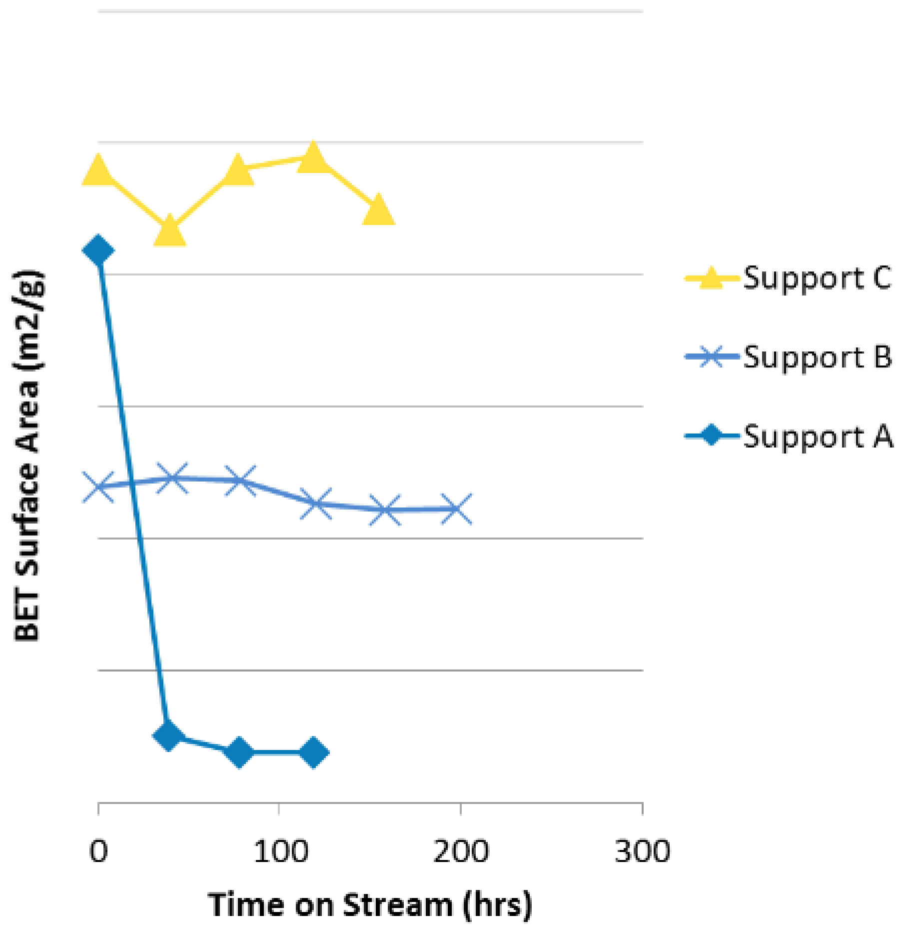
  - Generation II HDO Catalyst Support
    - Virent has identified a class of materials that is lower cost and easier to manufacture
    - Currently proving reactivity and stability within the process.

  - Generation II DHOG Catalyst
    - Virent has identified several classes of materials that provide lower costs and are easier to manufacture
    - One of these materials will be used in the final validation.

Generation II HDO Catalyst Support

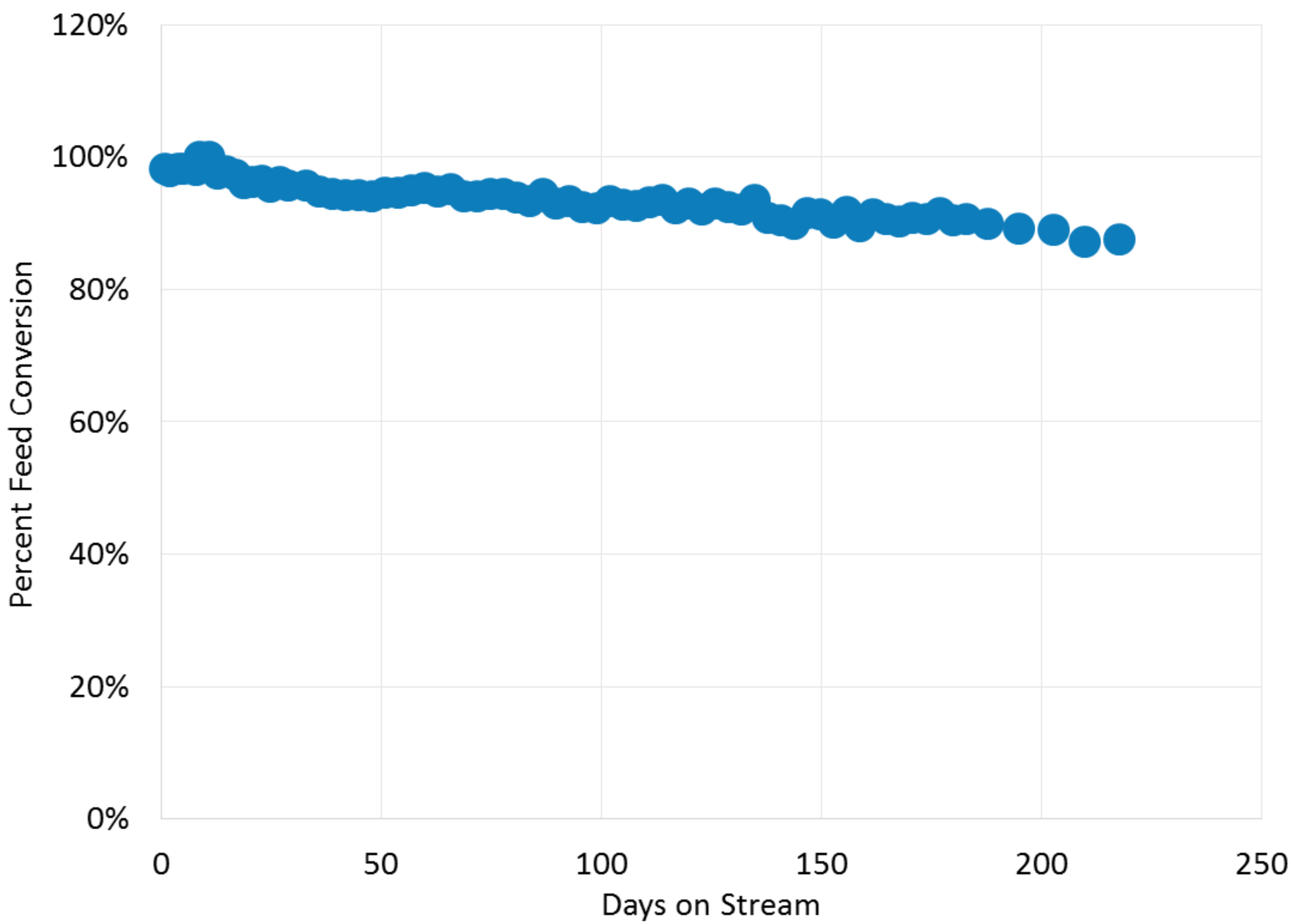
Continued development of catalyst supports and metal sets

- Focused development on catalyst cost reduction and commercialization
- Developed new protocol/method for accelerated aging tests
- Material class has potential for lower cost, greater availability, and ease of manufacturing

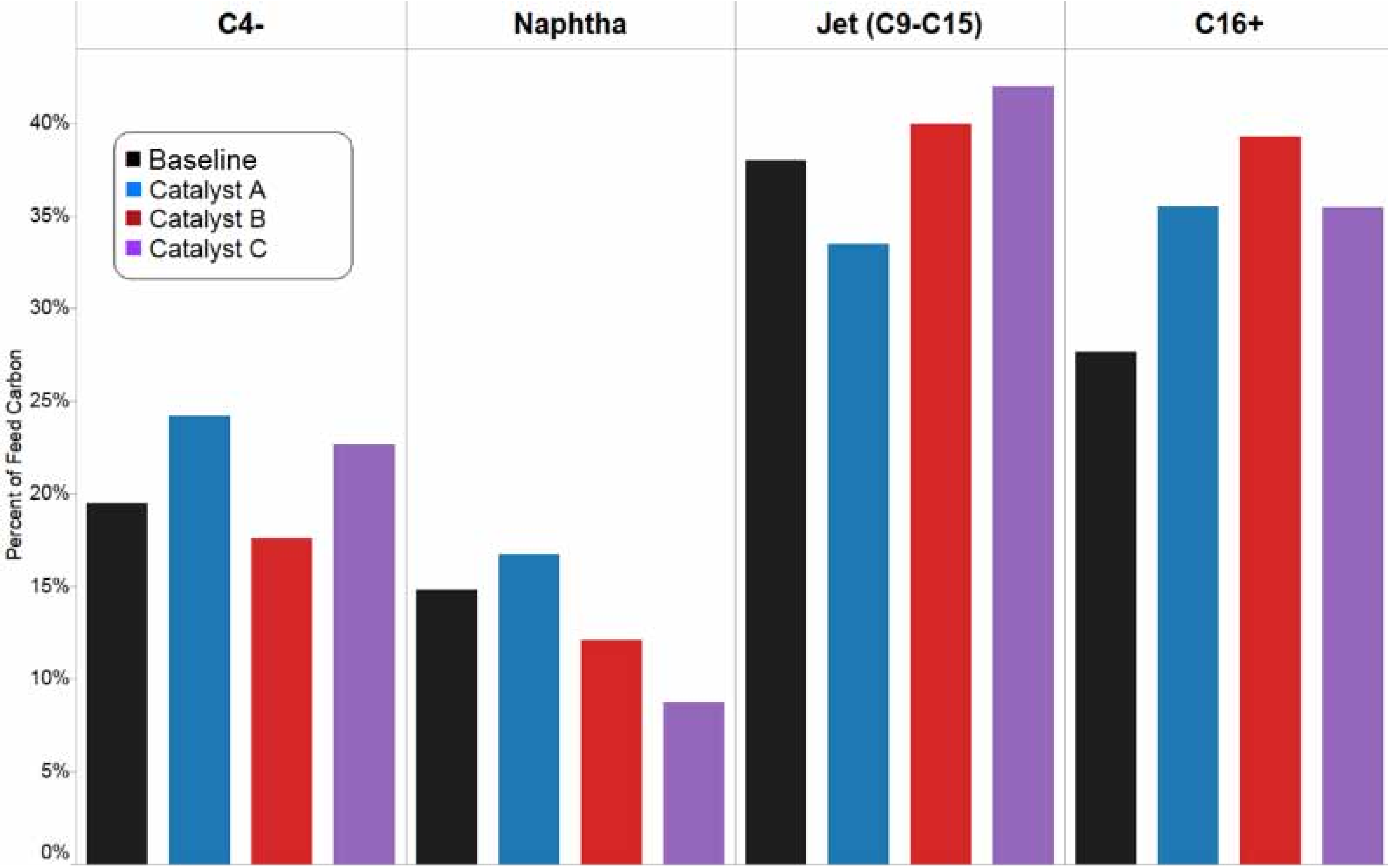


HDO Stability Run

Formulation with Generation II catalyst support and lower cost active metals



DHOG Catalyst Cost Reduction



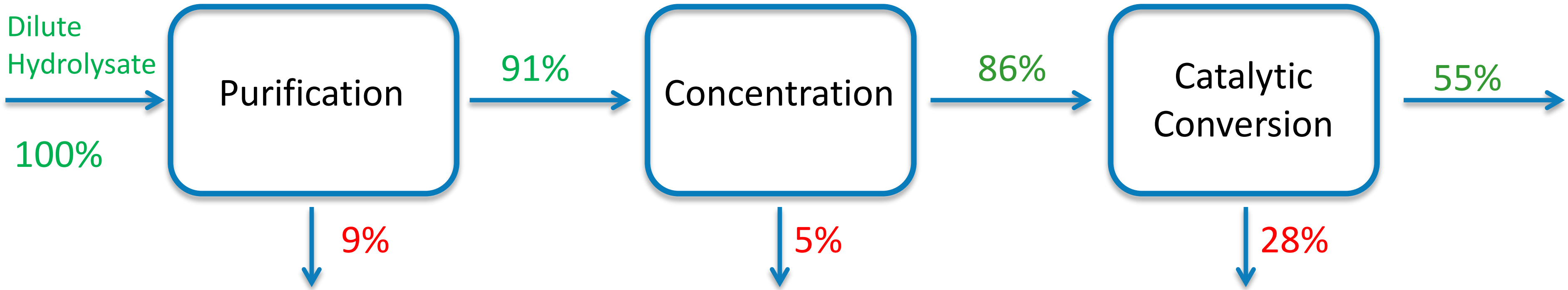
- 20+ catalysts screened
- Several catalysts increased production of Jet Range hydrocarbons, C9-C20
- Final validation will utilize lower cost DHOG catalyst formulation

Improved Carbon Recovery

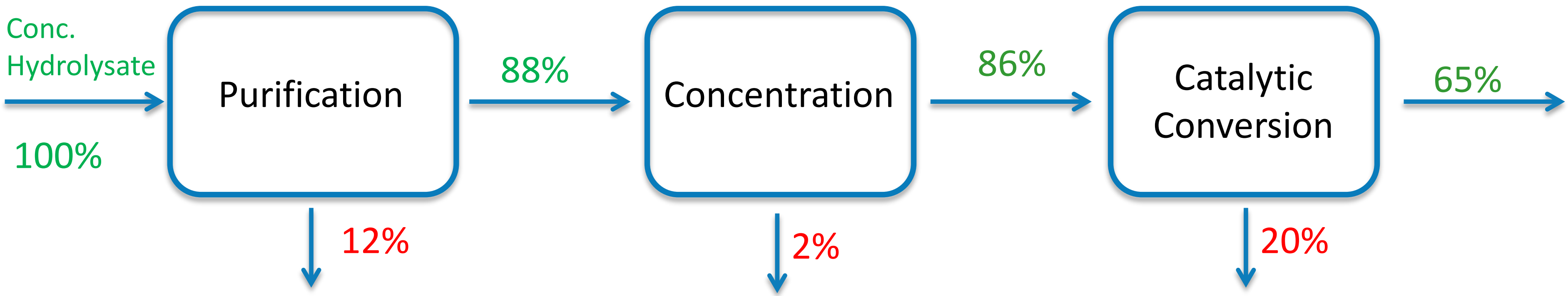
Green = carbon retention

Red = carbon loss

Benchmark Repeat:



Intermediate Validation:



4 – Relevance

- Contributions to meeting the platform goals and objectives of the BETO Multi-Year Program Plan
  - Biochemical and feedstock interface activities to determine desirable ash removal specification of targeted feedstock (corn stover).
  - Biochemical and chemical conversion interface activities to improve carbon yields to desired hydrocarbon products (Jet Fuel).
  - Improvement of production costs through minimization of enzymes, clean-up of resulting hydrolysate, reduction of catalyst cost, improved catalytic reactor performance, and increased catalyst lifetime.
  - With further improvement, it is believed that this technology route could meet conversion cost goals of $3.30 GGE by 2017.

- Applications of the expected outputs in the emerging bioenergy industry
  - Results from this project provide technical viability of combining a biochemical conversion technology front-end with a chemical (catalytic) conversion technology to generate “direct replacement” hydrocarbons from a lignocellulosic feedstock.
  - Process could utilize other front-end technologies similar to the NREL approach that are currently being demonstrated at commercial or semi-commercial scale.
  - Project has resulted in at least 5 US Patent applications.

5 – Future Work

- Project Ends April 2015
- Final Validation Scheduled for Early April (2015)
- After Validation, Final Reports will be Prepared

Project Summary

- Combined Biochemical/Chemical (BioForming) Process
  - Feedstock flexible process for the production of liquid fuels
  - Could be extended to hydrolysates generated from a number of other biochemical technologies currently being demonstrated at commercial or semi-commercial scale
- Process and TEA Improvements
  - Ash Reduction in the field, during deconstruction, and processing
  - Improved liquid fuels yield and jet fuel selectivity
  - Lowered catalyst cost
- Fungible Biofuels
  - Virent jet fuel meets preliminary testing for JP8 and military specs at high blend levels
- Project Completion April 2015
  - Final Validation the first of April 2015

Additional Slides

Responses to Previous Reviewers' Comments

- Response to Questions/Criticisms from 2013 Peer Review
  - Question: "How do they segregate the DOE-Funded Aspects of the project from other DOE-Funded projects"
  - Response:
  - To better distinguish the differences under this project (2.3.1.8) versus our NABC work:

    Under this project (2.3.1.8), corn stover is sourced by INL and then pretreated/deconstructed by NREL. We then apply purification/conditioning and catalytic conversion technology to make a distillate rich fuel stream. One of the project goals is to maximize the percentage of high quality jet fuel and good progress is being made. Diesel and gasoline cuts are also made as byproducts.

    Under the separate NABC project we are receiving deconstructed feedstock materials (corn stover and pine materials) from NREL and Washington State. We apply purification/conditioning steps and then a different set of catalytic conversion steps to make a very different fuel--an aromatic-rich gasoline blend stock. This gasoline blend stock is very different than the gasoline range byproduct produced via our distillate technology.

    We coordinate with our partners and segregate feedstock and other research material lots carefully to be sure the right materials are being used on the right projects. Further, all labor resources and other charges are uniquely applied to the correct project.

Go / No-Go Reviews

- Stage-Gate Review – February 2014
  - Four External Reviewers
  - Decision to Reduce Scope
    - NREL
      - No additional R&D work, provide only hydrolysate to Virent
      - Provide support for TEA
    - Virent
      - Continue Process Work with Hydrolysate provided by NREL
      - Final Validation in April

Publications, Patents, Presentations, Awards, and Commercialization

- Publications
  - Stickel, J. (2014, November)Flocculation assisted clarification of enzymatically hydrolyzed corn stover slurries. AIChE Annual Meeting. Atlanta, GA.
- Patents
  - Kania et al. 2013. Production of Distillate Fuels from Biomass-Derived Polyoxygenates. Patent Pending, filed March 15, 2013.

Deconstruction – Final Case

(NREL)
Acid
Impregnation
($60^{o}C$, 2 hours,
5% TS, 0.8% acid)

(NREL)
Acid Pretreatment
(NREL LHR, $160^{o}C$,
10 min)

(NREL)
Enzymatic
Hydrolysis ($50^{o}C$, 3
days, 20 mg/g*)

(NREL)
Solid/Liquid
Separations

(NREL)
Concentration
to 40-50% DS

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.
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.
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) and others.
Emerging Competitive Technologies	Monitor competitive landscape and continue to expand IP portfolio.

Large Addressable Market Sizes

The ultimate market for any biofuel is the national and global refined product markets, which collectively represents over a trillion dollar business. In these markets, the US consumes significant amounts of liquid transportation fuels with a large portion derived from imported crude oil.

Fuel Type	Current Consumption in 2012 (MMGPY)[1]	Projected Consumption in 2040 (MMGPY)	CAGR (%) 2012 – 2040
Motor Gasoline	133,378	101,373	(1.00%)
Jet Fuel	21,845	24,369	0.50%
Distillate Fuel Oil	59,772	70,836	0.80%

DOD Fuel Requirements[2]	FY 2012 (MMGPY)	Product Cost ($MM)
Jet Fuel	3,521	11,842
Distillates and Diesel	865	2,764
Totals	**4,386**	**14,606**

1) EIA Annual Energy Outlook 2014 Early Release Reference Case
2) DLA Fiscal Year 2012 Energy Facts. http://www.energy.dla.mil/library/Pages/Publications.aspx