U.S. Department of Energy (DOE) Bioenergy Technologies Office (BETO) 2017 Project Peer Review

One-Step High-Yield Production of Fungible Gasoline, Diesel, and Jet Fuel Blend Stocks from Ethanol without Added Hydrogen

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Thermochemical Conversion

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Technology Goal: High Yields of Liquid Hydrocarbons from Ethanol at Pilot Scale for Commercialization

5-100% Ethanol

Heat Exchanger → **Catalyst** → **Decanter**

Fractionation (as needed)

Chemicals, e.g., BTEX

Jet Fuel

Diesel

JP-8

Gasoline

Overcome ethanol blend wall and open up new ethanol markets

Existing infrastructure

Goal Statement

- **Project Goals:**

  1) Increase Yields: Increase hydrocarbon liquid (C5+) yields for ethanol-to-hydrocarbon catalytic technology initially developed by Oak Ridge National Laboratories (ORNL)

  2) Scale-up: Provide engineering design basis from which to scale-up to commercial operations,

  3) Technology Advancement: TRL 3 to TRL 5.

- **Project outcome:**

  1) Drastically Changes Biofuel Landscape: Opens up ethanol to HC market

  2) Ethanol Producer Flexibility: Producers can now make

  - **Gasoline blend stocks** that eliminate the ethanol "blend wall,"
  - Diesel and jet fuel blend stocks that expand fuel markets, and
  - Higher value chemical coproducts (BTEX – benzene, toluene, ethylbenzene, and toluene) that can improve process economics, particularly when fuel prices are low.

  3) Worldwide Adoption: Sustainable conversion of cellulosic ethanol into fuels and chemicals with GHG reduction potential of +95% while significantly reducing fossil fuel dependence.

Yields increased from 36% (initial) to >80% while scaling up operation 300x

Quad Chart Overview

Timeline

- Project start date: November 15, 2015
- Project end date: December 22, 2017
- Percent complete: 60%

Budget

	Total Costs FY 12 –FY 14	FY 15 Costs	FY 16 Costs	Total Planned Funding (FY 17-Project End Date)
DOE Funded	0	0	807	1,189
Project Cost Share (Comp.)*	0	0	323	477

Total Project: $2,796K

Barriers

- Technical barriers
  - Technical Risk of Scaling (*It-C*)
  - High Risk of Large Capital Investments (*Im-B*)
  - Efficient Catalytic Upgrading to Fuels and Chemicals (*Ct-H*)
  - Cost of Production (*Im-D*)
- Addressing Technical Barriers
  - Working with catalyst experts that guarantee scale-up 1,000,000x
  - Simple Bolt-on (1/10th CapEx)
  - High yields to both fuels and chemicals
  - High value chemical co-product decreases OpEx

Partners

- TechnipFMC (60%) – catalyst scale-up experts with many lab to commercial operation example
- ORNL (15%) - CRADA in place for new technology licensing

1 - Project Overview

- History
  - Oak Ridge developed catalyst to convert ethanol into hydrocarbons.
  - Vertimass recognized its importance and applied for license.
  - Vertimass was awarded license in 2014 in competitive solicitation.
  - Vertimass won DOE funding to accelerate scale up.
- Among biomass derived fuels, ethanol is the major success story.
  - Now added to gasoline to meet EPA RFS requirements.
  - However, market is limited to ~10% due to "blend wall" unless flex-fuel vehicles (FFV) or E15 have greater market penetration.
- Catalytic conversion of ethanol to hydrocarbon blend stocks overcomes (or bypasses) the blend wall.
- Working with TechnipFMC pilot plant to increase liquid yields and provide engineering data for commercial scale implementation.
- Goal is to become cost competitive with petroleum fuels.

2 – Approach (Management)

- Project Structure
  - **Vertimass:** Overall management of the project activities, schedule, and budget to achieve technical goals. TechnoEconomic Analysis (TEA) lead.
  - **TechnipFMC:** Pilot scale-up experimental operations, providing technical data and scale-up expertise to reach overall technical goals.
  - **Oak Ridge:** Transferring historical run data, catalyst preparation, continue development at smaller scale (effects of water co-feed)

- Management Approach
  - Weekly coordination meetings with ORNL (conference), TechnipFMC (Weymouth MA pilot), and Vertimass (conference).
  - Quarterly meetings with ORNL, TechnipFMC, and Vertimass.
  - Monthly conference updates with DOE and quarterly reports on progress and budgets.

2 – Approach (Technical)

- Technical Approach
  - **Scale-up Experts:** Capitalizing on TechnipFMC's 40+ years experience in scale-up from their pilot plant (Weymouth, MA) to commercial operations
  - **Parametric Examination:** Varying temperature, pressure, space velocity and catalyst formulations to maximize yields of liquid hydrocarbon blend stocks from ethanol at pilot scale.
  - **TechnoEconomic Model:** Production cost reductions as a function of technical progress (highly dependent on liquid yields)

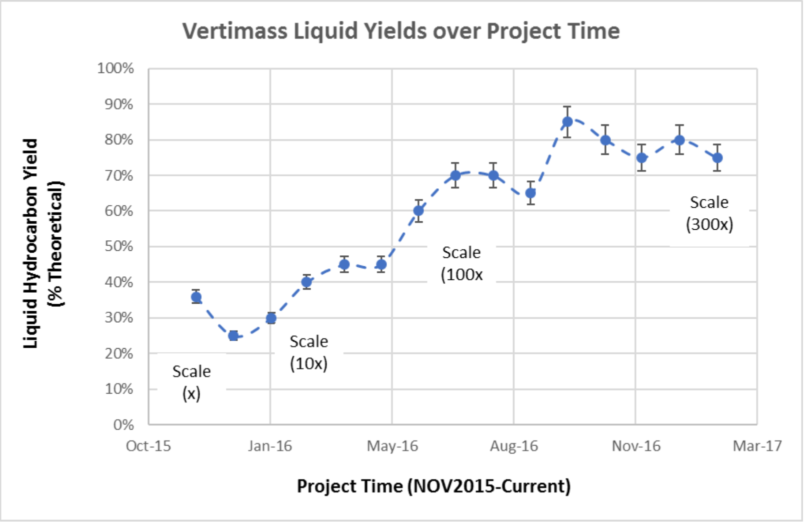
- "Go / No-Go" Decision Points
  - Confirm catalyst performance (TechnipFMC isothermal to ORNL). 36% HC_L ✓
  - Confirm catalyst production and performance ✓
  - Complete Design Basis Memorandum

- Top 3 challenges to commercial success
  - Achieving high liquid yields with commercial catalyst formulation
  - Qualifying product for blending with gasoline, diesel, and jet fuels
  - Confirming commercial catalyst durability

- Critical success factors
  - High liquid yields with commercial catalyst formulation.
  - Engineering design basis for integration into ethanol plant.
  - Partnerships with first adopters

3 – Technical Accomplishments

- **Technology: S**uccessfully transferred from ORNL to TechnipFMC
- **High Yields:** Increased liquid hydrocarbon yields (C5+) from 36% (initial validation) up to ~80% in 8 months
- **Scale-up:** 300x scale-up in 12 months while increasing to these high yields
- **Stoichiometric conversion:** 100% conversion of ethanol to HCs and water confirmed from ORNL to Technip
- **No external hydrogen**
- **Mild Conditions:** Low temperature (350 ºC) and pressure operations (60 psi) operations.
- **Wet ethanol feedstock:** 5-100% ethanol concentrations on V-ZSM-5 at ORNL have minimal effect.



3 – Technical Accomplishments (cont)

- Progress on Key Technical Targets (to drive costs lower)

Key Preformance Indicator (KPI)	Units	Initial Validation	Intermediate Target	Current	
Total HydrocarbonYield (HC_T)	g total hydrocarbons / g EtOH	0.55	0.55	0.55	✓
Hydrocarbon Liquid Yield (HC_L)	g C5+ hydrocarbons/g EtOH	0.22	0.50	0.45-0.50	✓
Hydrocarbon Gas Yield (HC_g)	g C1-C4 hydrocarbons/g EtOH	0.33	0.05	0.05-0.10	✓
Scale of Operations	mL EtOH / hr	0.40	120	80-120	
Temperature	Degrees Celsius (C)	350	325-375	350	✓
Space Velocity	LHSV (1/hr)	1.20	1.20	1.6-2.4	✓
Catalyst Loading level	g catalyst / mL/hr EtOH	0.50	0.50	0.50	✓
Stability	hours on stream before regen	6.0	16	15-20	✓
Regen Method	Air / Oxygen	Air	Air	Air	✓

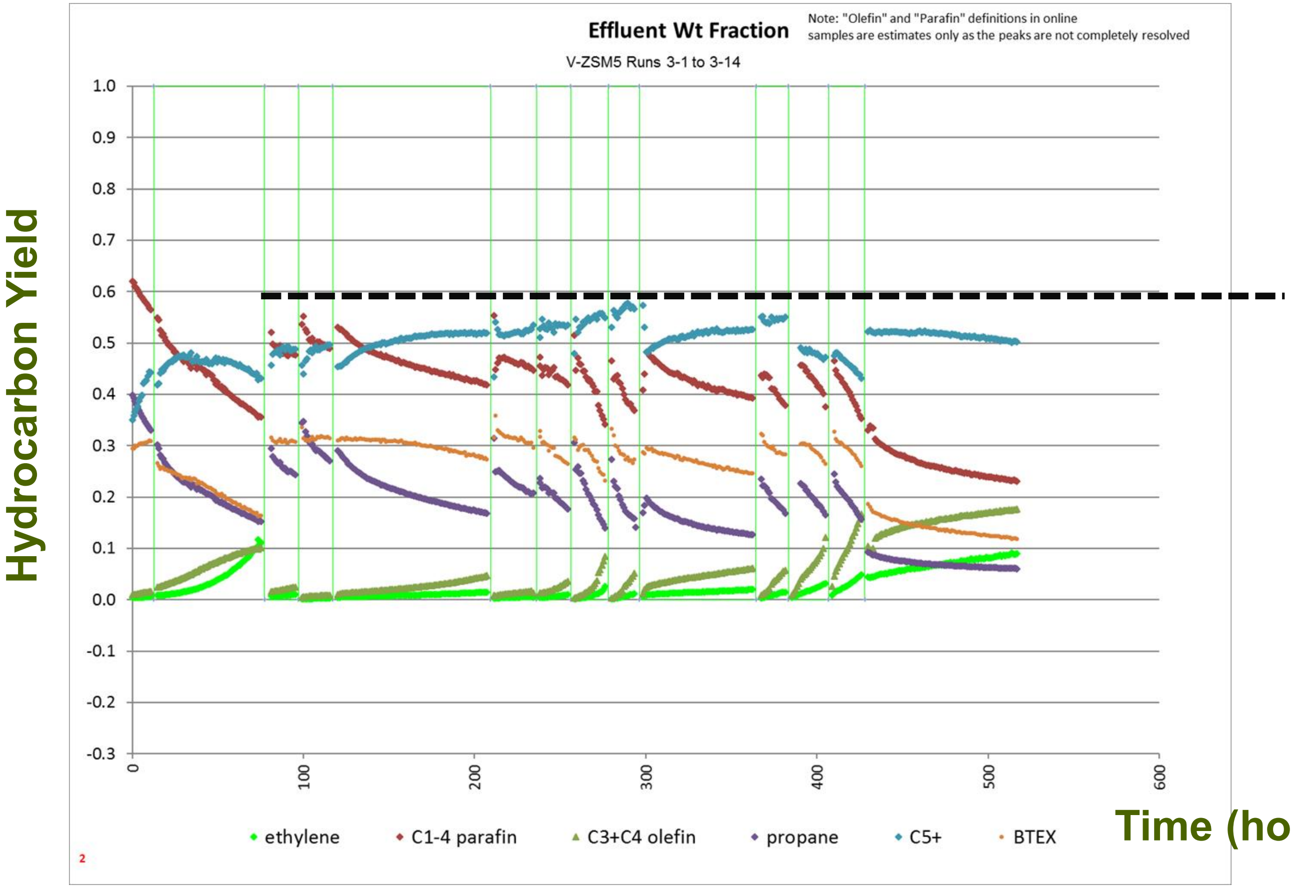
- Progress on Key Milestones
  - Determine effects of water cofeed & evaluate water product at lab scale ✓
  - Optimize catalyst regeneration cycle times ✓
  - Isothermal operation for process and catalyst characterization ✓

    Intermediate Validation – Stage Gate (scheduled week March 13th 2017)
  - Development and validation of robust industrial catalysts (In progress)
  - Adiabatic operation and prepare Design Basis Memorandum (after stage gate)
  - Integrate catalyst into ethanol production and optimize cost estimates via TechnoEconomics and Life Cycle Analysis (in progress)

3 – Technical Accomplishments (cont)

- **Key Finding 1:** Initial technology / catalyst (V-ZSM-5) maximum liquid yields plateaued at 60% one pass, 70% with recycle. Thus needed another solution.

Example Run
V-ZSM-5
(3-1 to 3-14)

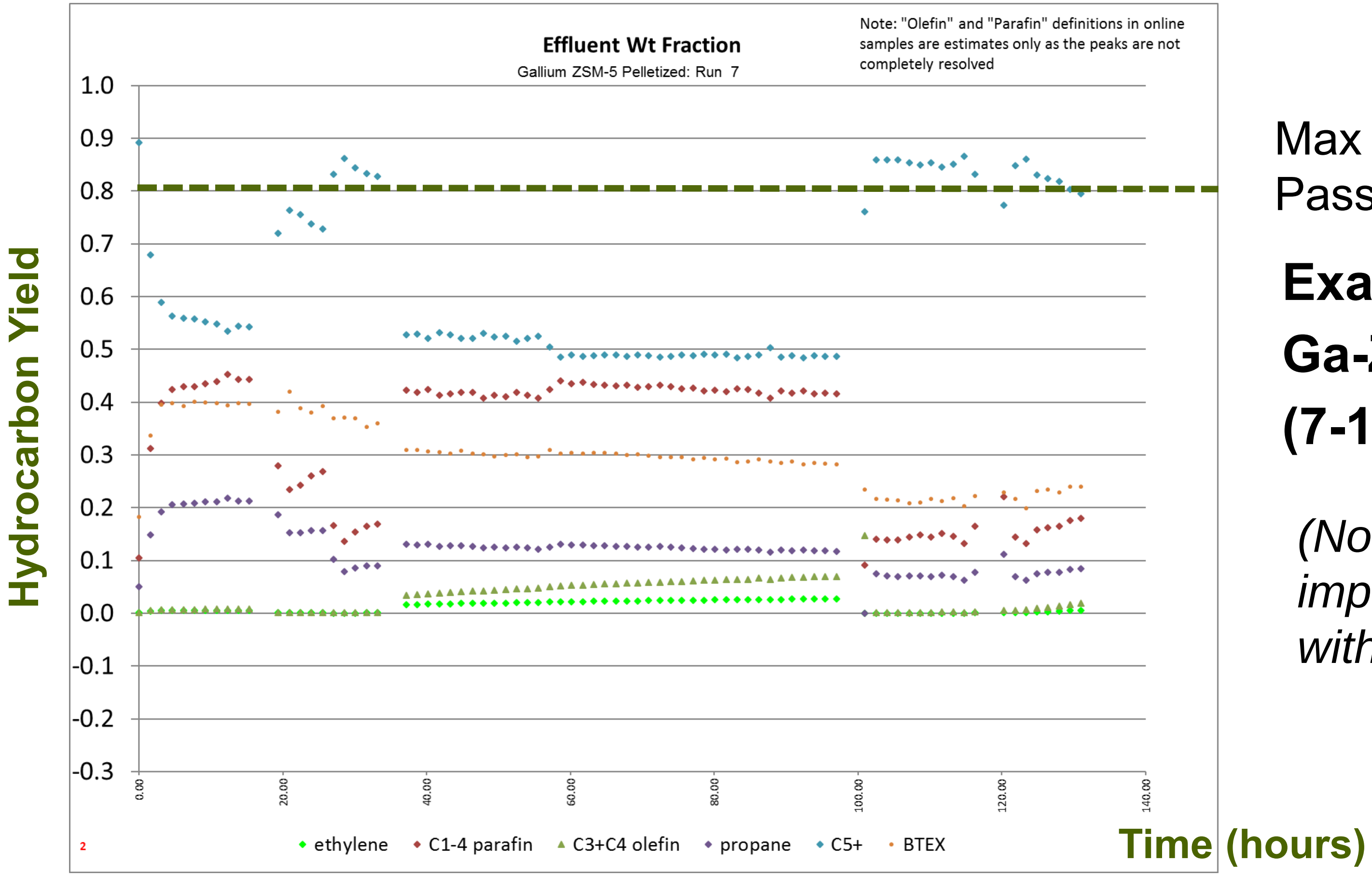


Max C5+ one Pass ~60%

(Max C5+ with Recycle ~70%, Appendix)

3 – Technical Accomplishments (cont)

- **Key Finding 2:** Moved to another catalyst (Ga-ZSM-5) in our license that offered higher yields (reached >80% one pass)



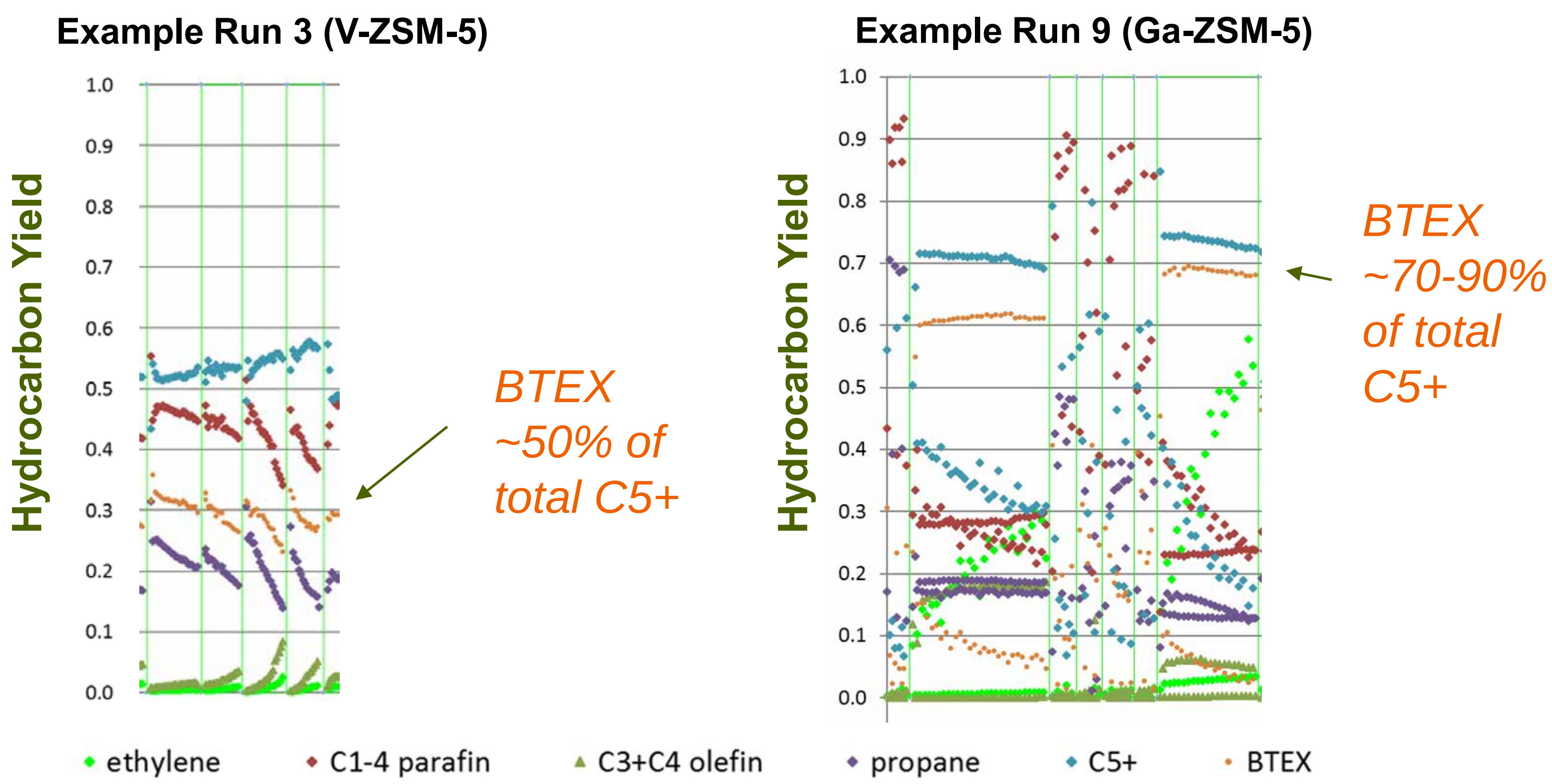
Max C5+ one Pass 80-85%

Example Run Ga-ZSM-5 (7-1 to 7-9)

(No statistical improvement with recycle)

3 – Technical Accomplishments (cont)

- **Key Finding 3:** Ga-ZSM-5 can produce higher levels of BTEX compared to V-ZSM-5 under at defined conditions
  - BTEX commands a premium over fuels (~70-80% higher value per unit volume).
  - This valuable co-product can be very important to reducing overall blend stock costs and improving competitiveness with low petroleum prices.



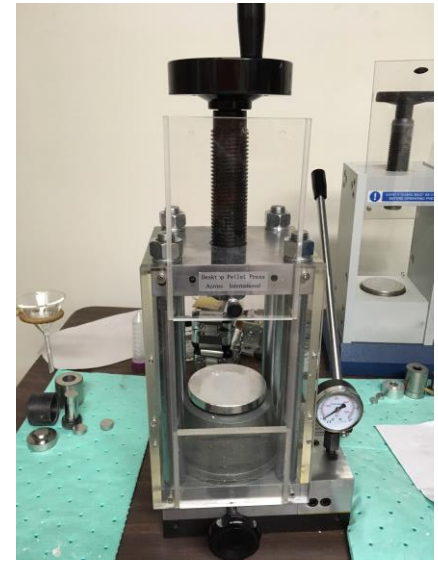
3 – Technical Accomplishments (cont)

Challenge

1) Needed more catalyst than ORNL could deliver
2) Reaching liquid yield targets
3) Powder catalyst channeling, high pressure drop
4) Reaching future final liquid yield target goals

Mitigation/Solution

1) Transferred catalyst production to TechnipFMC (accelerated production)
2) Parametric investigation boosted liquid product
3) Pelletized catalyst (new protocol)
4) Identified several additional approaches to increase yield from ~70% to target >82%



3 –Accomplishments (other)

Pathway to Commercialization

- **Commercial catalyst provider:** Working with catalyst manufacturer to employ Vertimass technology in their commercial catalysts for achieving scale-up goals.
- **Ethanol engineering firm:** Working with experienced engineering firm to define how Vertimass bolt-on can best integrate into starch and cellulosic ethanol facilities (e.g., heat integration, water usage).
- **First Ethanol Adopter:** LOI with commercial ethanol producer for first Vertimass commercial bolt-on
- **Life-Cycle Analysis (LCA):** Life Cycle Associates (Stefan Unnasch) performed initial LCA on our process resulting in CO_2 sequestering potential with high carbon intensive BTEX products – this could shift starch ethanol producers into 50%+ GHG reduction (conventional to advanced) *(Preliminary results and subject to EPA review)*

4 – Relevance

- **Project Goals:**
  1) Increase Yields: Increase Hydrocarbon liquid (C5+) yields for ethanol-to-hydrocarbon catalytic technology initially developed by Oak Ridge National Laboratories (ORNL) to support cost effective commercial implementation,
  2) Scale-up: Provide engineering design basis from which to scale-up to commercial operations,
  3) Technology Advancement: TRL 3 to TRL 5.
- **Importance:** Potential to drastically change biofuel landscape
  Commercialization eliminates ethanol blend wall, expands ethanol markets to fungible diesel and jet hydrocarbon blend stocks, further diversifies product slate to chemicals, and reduces GHGs.
- **Relevance to BETO Multi-Year Program Plan:** Technology directly addresses relevant barriers and overall MYPP goals
- **Relevant to the bioenergy industry:** Vertifuel eliminates blend wall and expands ethanol penetration to massive fuel and chemical markets.
- **Advances to state of technology**: Low temperature and pressure operation, no external hydrogen, low % light products, high liquid yields.

5 – Future Work

- Employ commercial catalyst and scale-up to larger pilot reactor to provide engineering basis for commercial scale-up (TechnipFMC can guarantee commercial scale-up from their large pilot).

Facility	Scale (x)
ORNL	x
Technip small pilot	300x
Tecnip large pilot	5,000 x
Commercial	1,000,000x

✓
✓

- Key Milestones
  - Intermediate validation (March 13-17, 2017).
  - Move to commercial catalyst supports.
  - Move to large pilot reactor.
- Upcoming Go/No-Go Points:
  - Commercial Catalyst Performance Q2 2017
  - Complete Design Basis memorandum Q4 2017
- Remaining budget (DOE $1,189k, Cost share $477k) appears adequate to complete remaining tasks.
- Vertimass is currently raising $8MM for Series B funding

Summary

- Vertimass ethanol to hydrocarbon conversion technology

  1) Major improvements in the technology over the last year

     - Boosted Liquid Yields from 36% to >80% in 8 months

     - Scaled-up 300x to date

  2) Industry Acceptance: LOI with ethanol producer for commercial plant

  3) Future Work: BETO funding for 2017 project steps will allow for this shift to commercialization

  4) Potential to drastically change biofuel landscape

Additional Slides

Patents & Presentations

- Patents (applications) through this work

1) US20160362612A1: “Systems and methods for reducing energy consumption in production of ethanol fuel by conversion to hydrocarbon fuels”
2) US 20160362612 A1: “Systems and methods for reducing water consumption in production of ethanol fuel by conversion to hydrocarbon fuels”
3) 62/315889: “Systems and methods for improving yields of high molecular weight hydrocarbons from alcohols”
4) 62/255022: “Systems and methods for improving yields of hydrocarbon fuels from alcohols

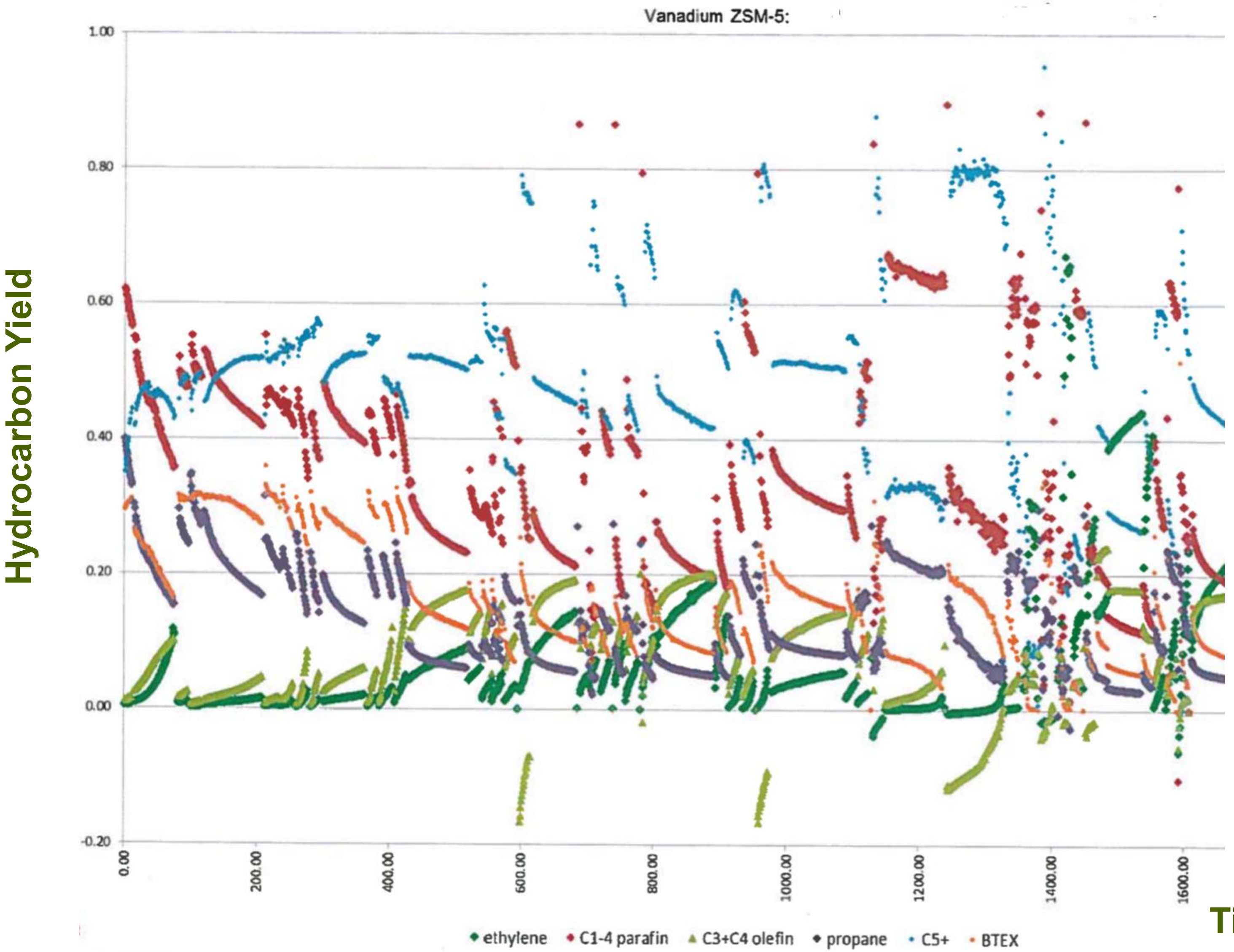
- Presentations

1) “Novel Vertimass Catalyst for Conversion of Ethanol into Renewable Jet Fuel and High Value Co-Products” Lux Executive Summit Americas, May 9-11 2016
2) “Single Step Ethanol Conversion to BTEX and Jet, Diesel, and Gasoline Blending Components” International Fuel Ethanol Workshop & Expo 2016

Vertimass Licensed Patents from UT-Battelle

Patent #	Patent Name	Issued Patent # / Application #
1	Zeolite-based SCR catalysts and their use in diesel engine emission treatment	US 8987161 B2
2	Hydrothermally stable, low temperature NOx reduction NH3-SCR catalyst	US 8987162 B2
3	Zeolitic catalytic conversion of alcohols to hydrocarbons	US 9533921 B2
4	Catalytic conversion of alcohols having at least 3 carbon atoms to hydrocarbon blendstock	US 9181493 B2
5	Catalytic conversion of alcohols to hydrocarbons with low benzene content	US 9434658 B2, US 9278892 B2

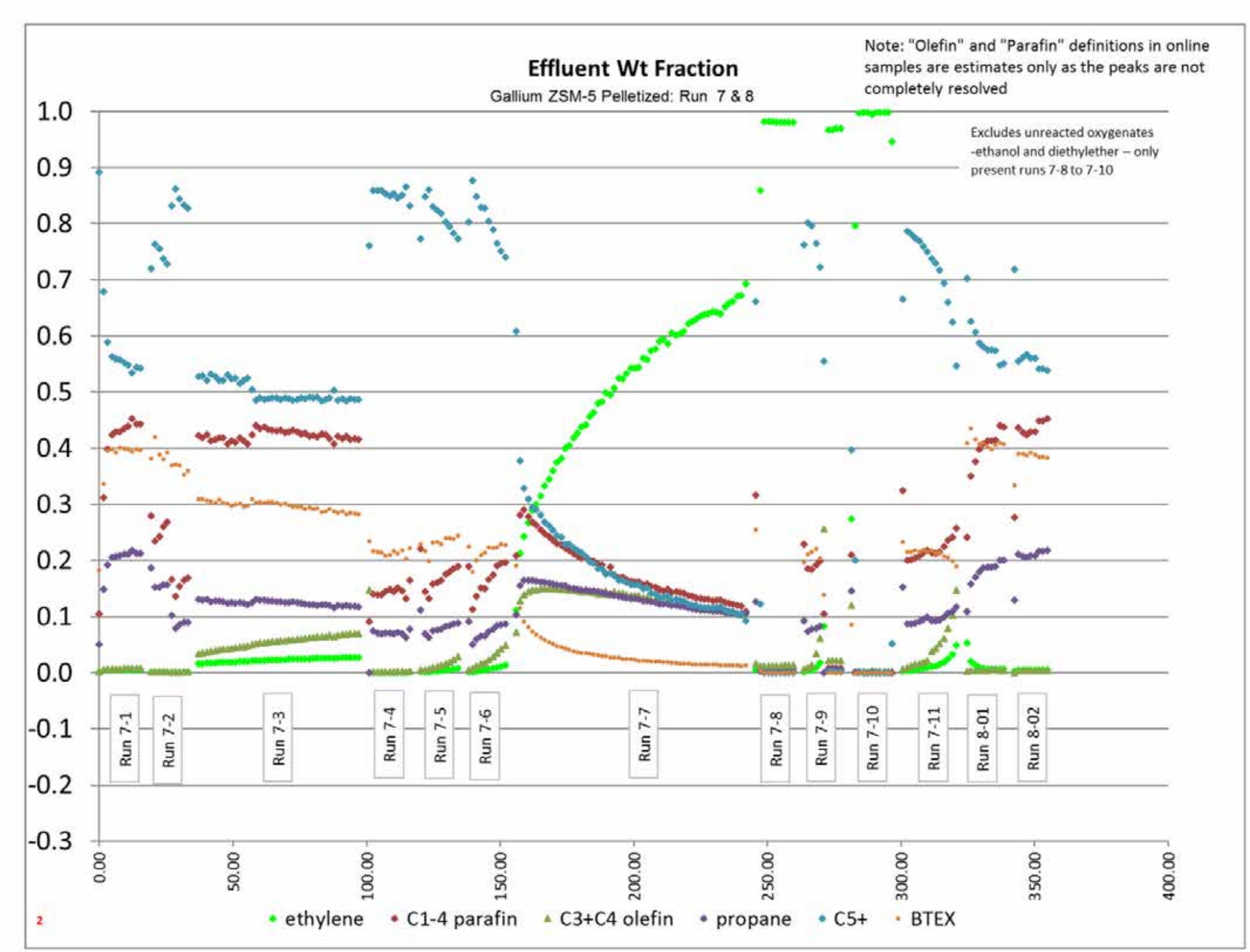
Ethanol Conversion on V-ZSM-5



Note: Olefins below 0% hydrocarbon yield represent mock feed recycle

Ethanol Conversion on Ga-ZSM-5 (Run 7&8)

Hydrocarbon Yield

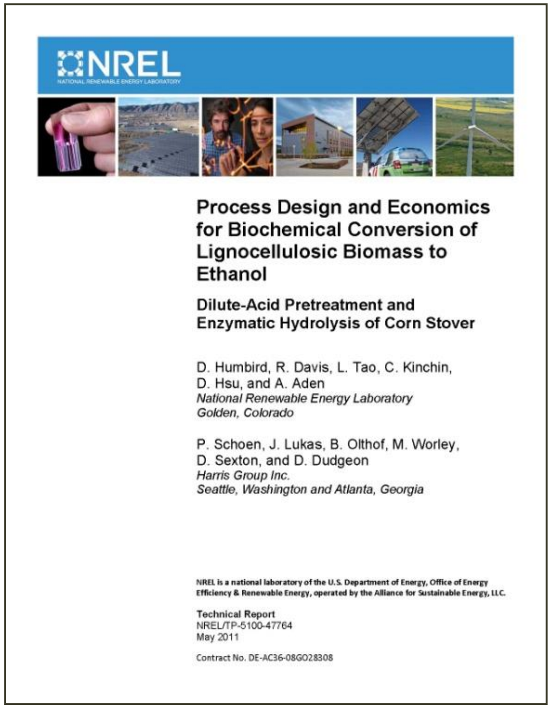


Time (hours)

TechnoEconomic Base Model

- Economics based on NREL research for biomass to ethanol steps (2011 Biochemical Design Report Update), ORNL research for ethanol to hydrocarbon step
- Assumes n^{th}-plant project cost factors and financing (ignores first-of-a-kind risks)
- Discounted cash-flow ROR calculation includes 10% IRR, interest, and income taxes
- Determines the plant-gate or minimum product selling price
- Baseline ethanol selling price is $2.15/gal ethanol (2007$) or $3.27/gal gasoline eq.
- Modeled conversions are based on anticipated pilot-scale performance in 2015

2011 Design Report Update


NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol

Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover

D. Humbird, R. Davis, L. Tao, C. Kinchin, D. Hsu, and A. Aden
National Renewable Energy Laboratory
Golden, Colorado

P. Schoen, J. Lukas, B. Olthof, M. Worley, D. Sexton, and D. Dudgeon
Harris Group Inc.
Seattle, Washington and Atlanta, Georgia

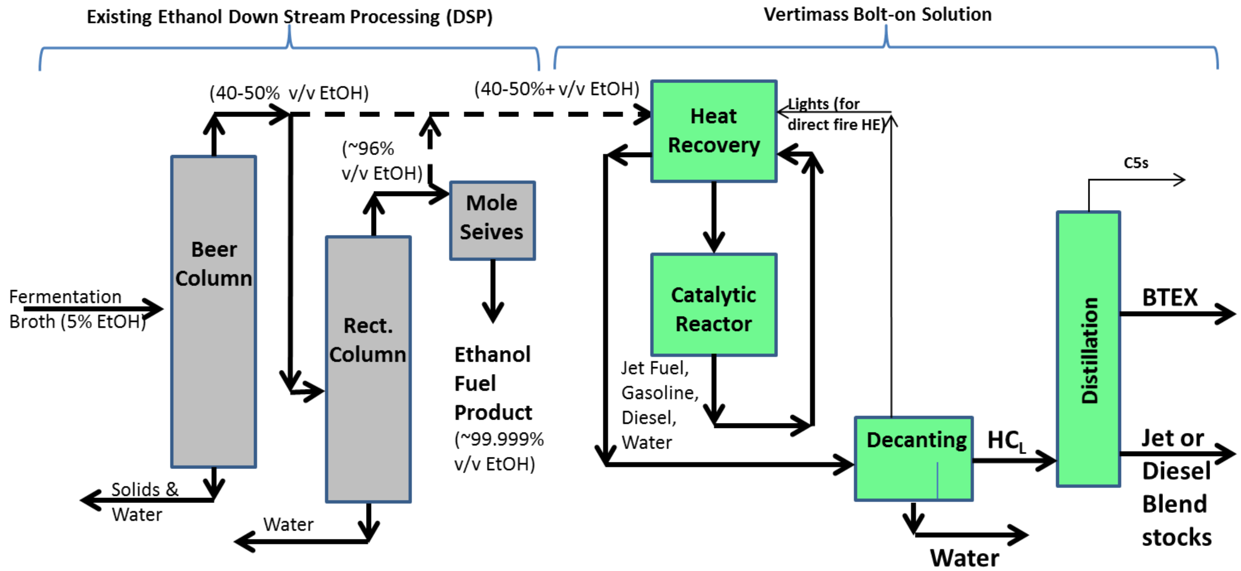
NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency & Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Technical Report
NREL/TP-5100-47764
May 2011

Contract No. DE-AC36-08GO28308

http://www.nrel.gov/docs/fy11osti/47764.pdf

TechnoEconomic Vertimass Model



- Excel based model
- Assumes product taken of rectification column to feed Vertimass bolt-on
- Includes heat integration of Vertifuel products into ethanol facility
- Capital costs for Vertimass bolt-on estimated
- Operating Costs (added to ethanol production costs) include catalyst costs, energy usage, insurance, taxes, maintenance, and labor.