

# Direct Catalytic Upgrading of Current Dilute Alcohol Fermentation Streams to Hydrocarbons for Fungible Fuels [2.3.1.100]

Chaitanya Narula,<sup>1</sup> Zhenglong Li,<sup>1</sup>  
E. Casbeer,<sup>1</sup> Robert A. Geiger,<sup>1</sup>  
James P. Szybist,<sup>2</sup> Martin Keller,<sup>2</sup>  
Brian H. Davison,<sup>2</sup> and Tim Theiss<sup>2</sup> (PI)

Oak Ridge National Laboratory

<sup>1</sup>Materials Science and Technology Division

<sup>2</sup>Energy and Environmental Sciences Directorate

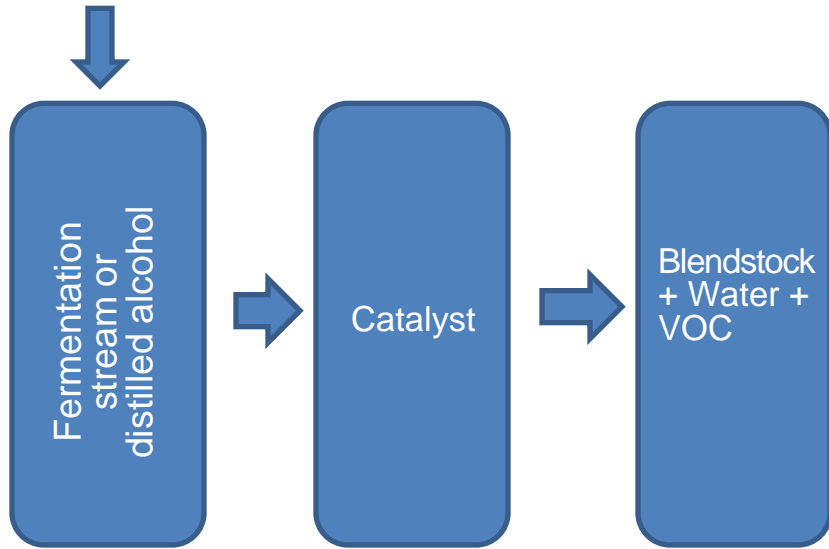
Technology Area Review: Biochemical Conversion  
2015 DOE Bioenergy Technologies Office  
(BETO) Project Peer Review  
March 24, 2015



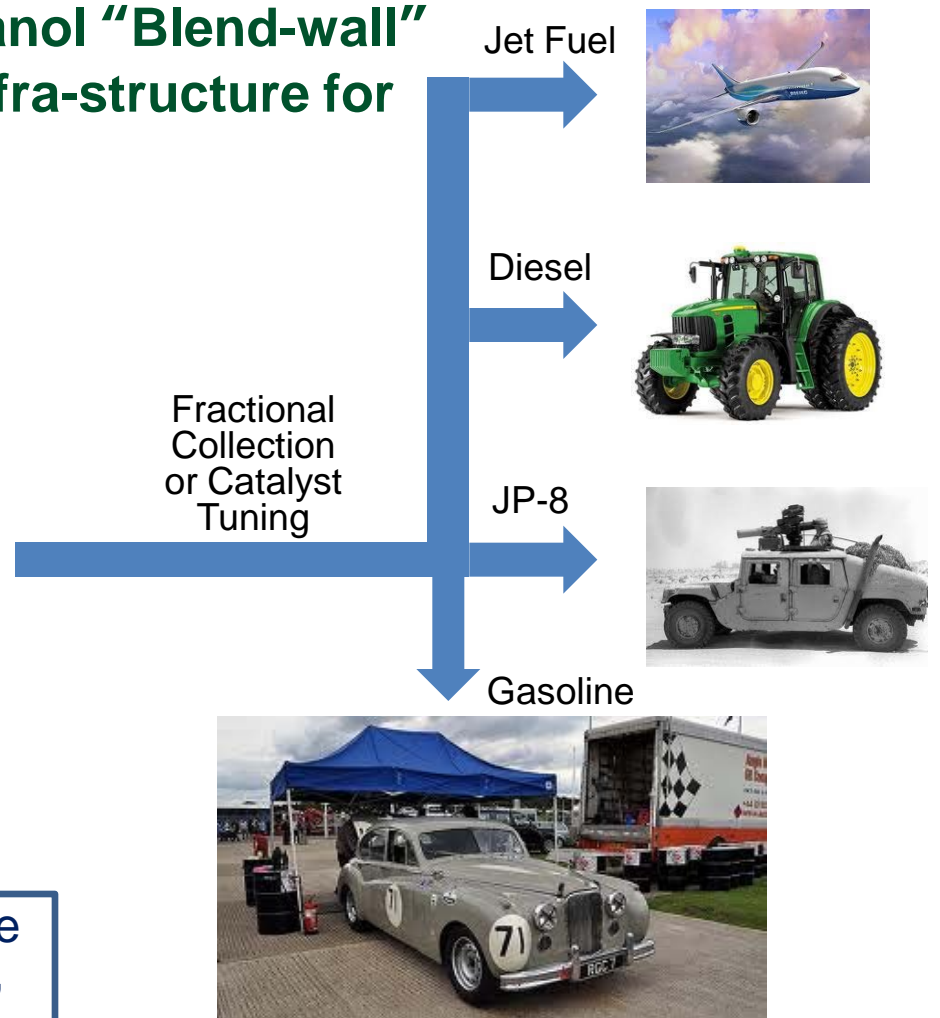
(This presentation does not contain any proprietary, confidential, or otherwise restricted information.)  
(The technology has been licensed to Vertimass LLC. CN, BHD, and MK are minority stock-holders of Vertimass.)

# Technology Goal - A General Platform for Converting Fermentation Streams to Hydrocarbon Blendstock

- Beyond the Ethanol “Blend-wall”
- Uses existing infra-structure for distribution”



Biomass derived fuels are highly desirable because they are from renewable source, reduce foreign oil dependence, and allow compliance with regulatory requirements



# Goal

- The program objective is to take the ethanol upgrading technology from TRL 2 to TRL 3-4 during the course of investigation.
- This is part of the BETO conversion goal in advanced biofuels
  - It is part of a novel biological/chemical conversion
  - It conserves carbon and hydrogen while upgrading
  - It may be certified to integrate into the petroleum infrastructure
  - Specific barriers:
    - Bt-I: Catalyst Efficiency
    - Bt-K: Product Acceptability and Performance
    - Bt-J: Biological Conversion Process Integration
- As an “add-on” technology, it will help increase markets for current and future cellulosic ethanol infrastructure by upgrading into fungible advanced biofuels (i.e., blendstocks for gasoline, diesel, and jet)
  - Specific barriers:
    - Im-C: High Risk of Large Capital Investments and
    - Im-H: Availability of Biofuels Distribution Infrastructure

# Quad Chart Overview

## Timeline

- Project start date: October 1, 2011
- Project end date: September 30, 2016
- Percent complete: 75%

## Budget

\$K	FY12 Start	FY13	FY14	FY15	FY16 end
DOE	150	400	500	500	200
Total project: \$1,750K					

## Barriers

- Overcoming blend-wall for biomass derived fuel with economically feasible process
  - Bt-J, Im-C
- Demonstrate catalyst durability
  - Bt-I
- Improve usable fuel quality
  - Bt-K, Im-H

## Partners

- Technology licensed to Vertimass, LLC (March 2014) for scale-up and fuel certification
- Ongoing collaboration with NREL for preliminary techno-economic analysis

# Project Overview

- History
  - Preliminary work under BESC and ORNL internal investment
  - FY12 BETO seed project
- Among biomass derived fuels, ethanol is a success story
  - It is added to gasoline to meet EPA regulatory requirements
  - However, its use is limited to ~10%. Use of ethanol beyond this “blend wall” requires Flex-Fuel Vehicles or use of E15 which have low market penetration
- Catalytic conversion of ethanol to hydrocarbon blend-stock overcomes (or bypasses) the blend wall at laboratory scale
- Our objective is to find and demonstrate a durable catalyst(s) that can convert ethanol in fermentation stream at any stage of purification to hydrocarbon blendstocks under moderate conditions. This will lead to blendstock being cost competitive with petroleum derived fuel.

# Approach (Technical)

- Our technical approach employs mechanistic studies to direct catalyst development for ethanol conversion to hydrocarbon blendstocks at lab scale.
  - We utilize non-precious metal catalysts on zeolites. Single metal and bi-metallic catalysts have been developed along with modified process conditions to result in different blendstocks.
- Success factors
  - Our major “go-no go” decision point was based on catalyst durability of >200h
  - Produced and analyzed 4 L of “gasoline” blendstock and 1 L of diesel/jet blendstock
  - A major ongoing driver is to further improve fuel quality to aide in fuel certification of each product as a blendstock for gasoline and/or diesel/jet end-uses



# Approach (Management)

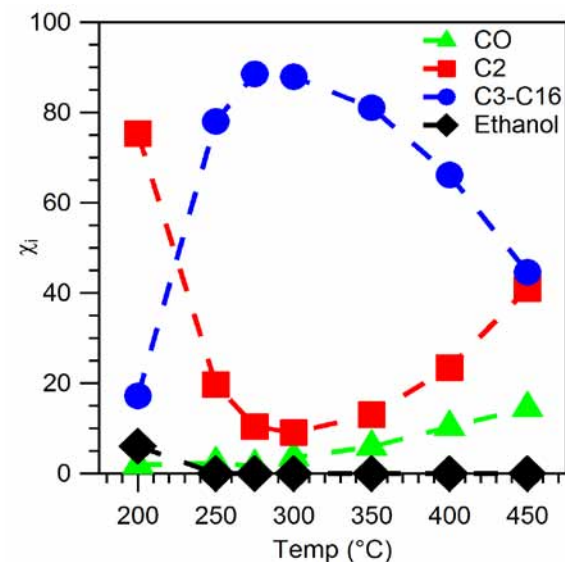
- Success factors
  - Develop IP portfolio
    - Patents submitted (3 so far)
  - License technology to Vertimass (March 2014)
    - Vertimass current goals are scale-up and fuel certification
- Challenges
  - Fuel certification may require improved quality
    - Communication with Vertimass in their efforts
- Key milestones are as follows:
  - Obtain experimental data for mass balance and heat of combustion of the produced blendstocks for energy balance data.
  - Update TEA based on FY14 data and energetics.
  - Reduce C2 (ethylene) to ~1% or less and C2+C3 to less than 5% at the laboratory scale. Confirm that coke production is a negligible percent.
  - Reduce BTX to below 15% with benzene below 0.68% (EPA regulatory requirement) and overall aromatics to ~40%.
  - Provide process data (energy and mass balance, reaction temperature and space velocity and product analysis) for detailed TEA.



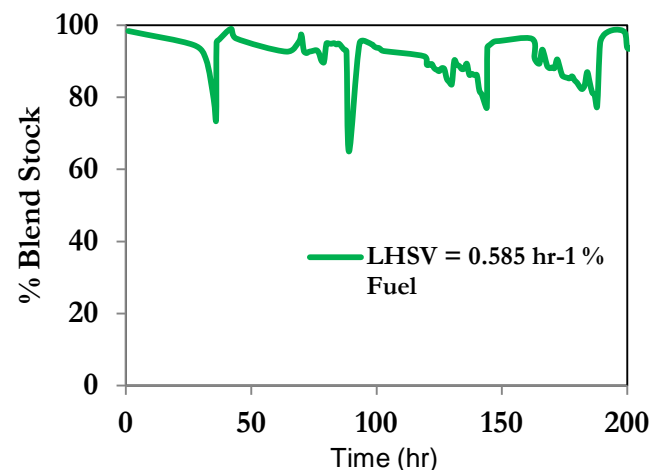
ORNL inventors (from left) Narula, Davison and Keller display the technology with Vertimass chairman William Shopoff (March 2014).

# Technical Accomplishments

- Catalytic conversion of ethanol to C<sub>3</sub> to C<sub>15</sub> blendstock
  - Stoichiometric conversion (100%) to HC and water
  - 350°C and atmospheric pressure
  - No added hydrogen
  - Durable catalyst (tested for >200h)
  - Water concentration had no significant impact of ethanol conversion process so direct ethanol fermentation streams could be employed
  - Actual fermentation streams and distillates converted to hydrocarbon blendstock
  - Engine experiments at ORNL show combustion similar to gasoline
  - Energy balance is slightly exothermic from estimate using HC of blendstock
- Heterobimetallic catalyst more versatile than monometallic one with improved selectivity



Constant LHSV of 2.93 h<sup>-1</sup>



Sample Catalyst Regeneration

- Comparable estimated costs

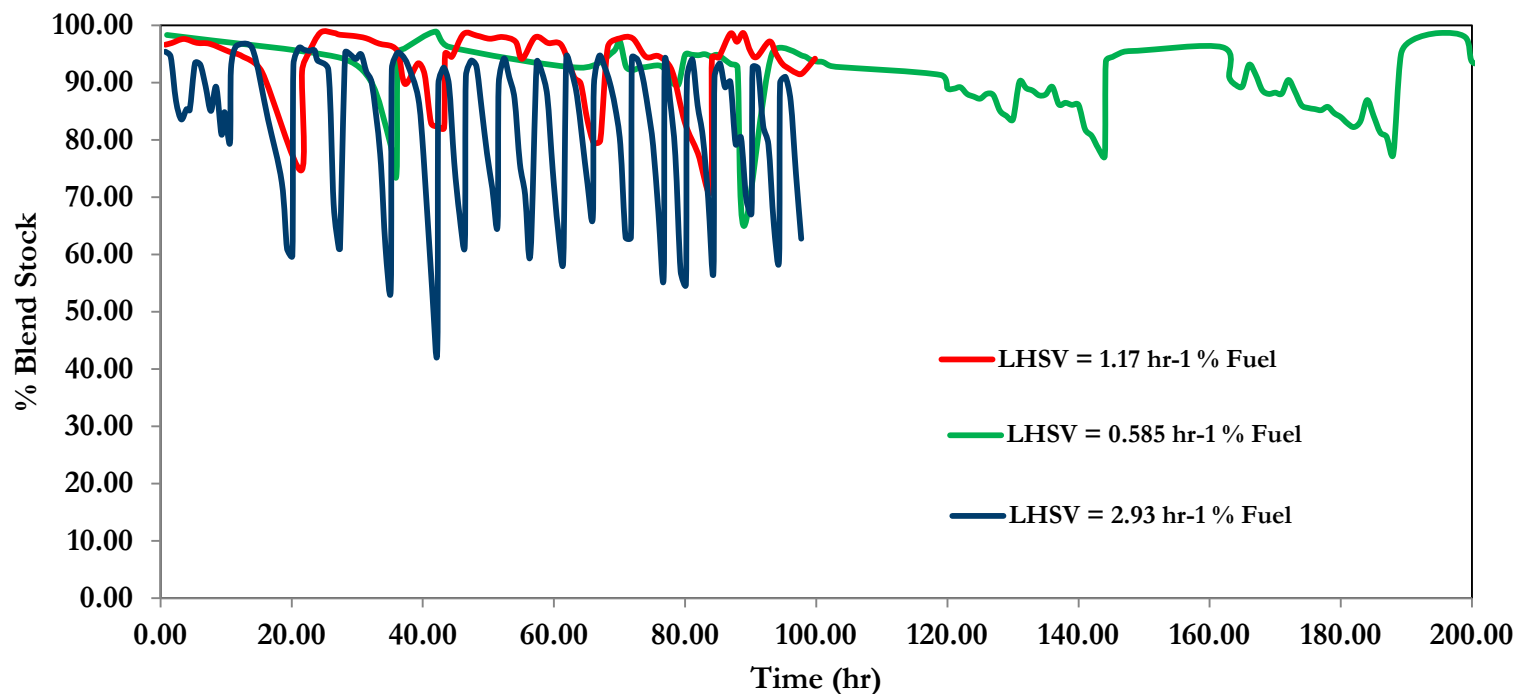


# Technical Accomplishments (2)

- BETO Project began TRL2; now TRL 3-4
- 2014 showed increased catalyst durability and produced test quantities
  - Demonstrated catalyst durability increase from 100 h under accelerated aging to >200h
  - Increased production from mL/d to >1 L/d
    - Produced 4L of gasoline blendstock for further testing. There was a minor challenge in scale-up of lab system due to safety reviews and condensate load with improved catalysts.
    - Produced 1L of a diesel-jet blendstock with a modified mixed zeolite catalyst
  - Previously showed novel hydrocarbon pool mechanism; this year improved energy and mass balances and optimal conditions
    - Demonstrated that reaction is slightly exothermic
- FY15 goals
  - Improve usable fuel yield and quality (decrease ethylene and control BTX)
  - Improve experimental estimates of mass and energy balances for TEA
    - Replace dehydration
    - Integrate into partial distillation



# V-ZSM-5 Durability >>200h Over Multiple Regeneration Cycles and No Deactivation



- V-ZSM-5 was operated at 350°C at a specified LHSV till C<sub>2</sub><sup>+</sup> formation started to fall due to apparent coking
- V-ZSM-5 was decoked by heating at 450°C and operation restarted
  - 200h at LHSV of 0.59 h<sup>-1</sup>
  - 100h at LHSV of 1.17 and 2.93 h<sup>-1</sup>

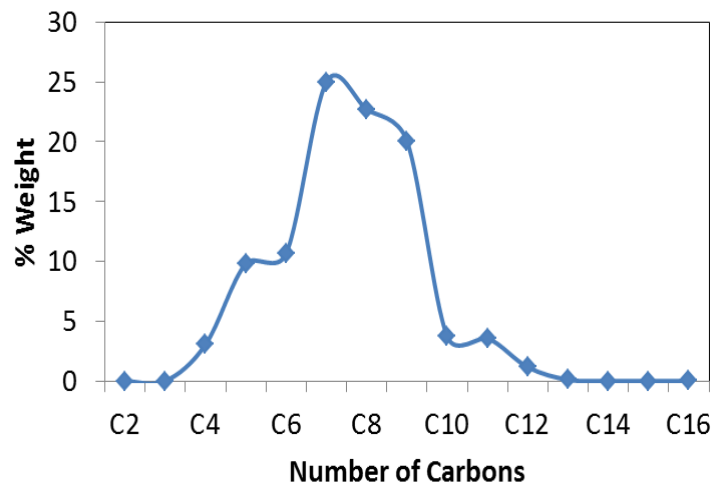
# Analysis of Blendstock

- Analysis at SGS North America, 1201 W 8<sup>th</sup> Street, Deer Park, Texas

- Boiling Range of ~30°C to 270°C
- Composition by % Vol of Group
- Total Calculated RON = 105.7
- Total Calculated MON = 88.9

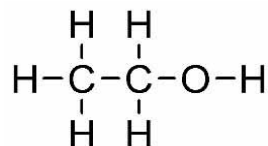
Calculated	Total
Avg MW	97.59
Avg SG	0.808
Avg API @ 15.6°C	46.8
RVP	5.14
Tot H	11.18
C/H	7.91
E200	34.3 %v/v
E300	88.39%v/v

**Fuel Properties**

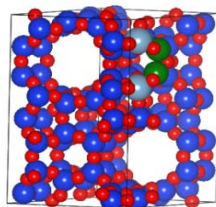


Group	% Volume
Paraffins	3.82
I-Paraffins	24.02
Olefins	6.51
Naphthalenes	5.41
Aromatics	60.2
Oxygenates	0.00

# Ethanol Upgrading Shows Novel Mechanism

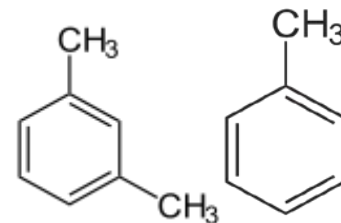


- Ethanol or fermentation stream



- Low-cost metal-exchanged zeolite catalyst: V-ZSM-5 or VIn-ZSM-5

- Aromatic and Aliphatic HCs typical of blend-stock constituents
- (C<sub>4</sub>-C<sub>15</sub>) with water and trace ethylene byproducts

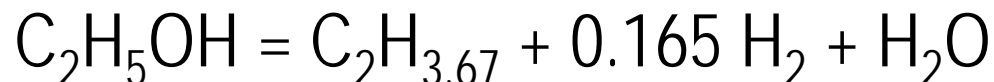


- C<sub>2</sub>H<sub>5</sub>OD Experiment
  - Deuterium incorporation in HC
- Ethylene (70%) + D<sub>2</sub>O (30%)
  - No deuterium incorporation in HC
  - Rules out deuteration of catalyst surface as the pathway to deuterium incorporation in the product stream
- Ethanol (70%) + D<sub>2</sub>O (30%) yields deuterium incorporation in all hydrocarbons *except* ethylene
- Rules out endothermic dehydration ethylene as the key step (as stated in the literature) and supports a hydrocarbon pool mechanism
- DRIFTS studies also offer support to a hydrocarbon pool mechanism

# Mass and Energy Balance

- Mass Balance

- Overall Equation



- Energy Balance

- Based on heat of combustion

- C2-C4 yield from GC after calibration
- C5 and C5+ analysis at SWRI, Texas

- -0.88 MJ/kg [Slightly exothermic]

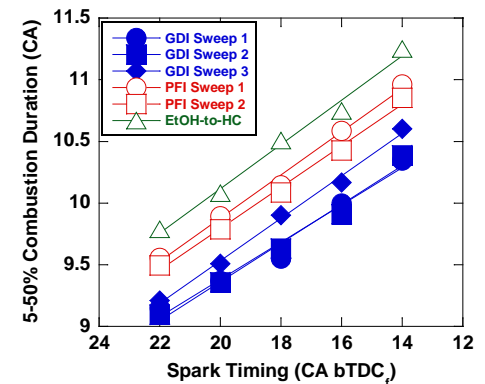
- Note: Ethylene route is +0.93 MJ/kg [endothermic]

- These results impact

- Mechanistic understanding for improvement and for IP
- Accuracy for TEA parameters

# Gasoline Blendstock Tested in Internal Combustion Engine with Comparable Performance

- A new capability has been added to the Sturman variable valve actuation engine which can now run at a fuel quantity as low as 250 mL Ported Fuel Injection (rail pressure 5 bar)
  - Engine was warmed-up using the gasoline direct injection fueling system with **UTG91** certification gasoline so that none of the sample experimental fuel was consumed
  - Constant fuel and air flow rate through spark timing sweep
    - Operating condition: 1500 rpm, nominal load of 8.1 bar IMEPg
    - 3 times with UTG91 with DI fueling system
    - Spark timing sweep conducted 2 times with UTG91 using PFI fueling system
    - Spark timing sweep conducted 1 time with EtOH-to-HC fuel
- Ethanol-to-HC fuel has slower combustion duration, largely due to decreased knocking propensity and high octane
  - Preliminary emissions comparable

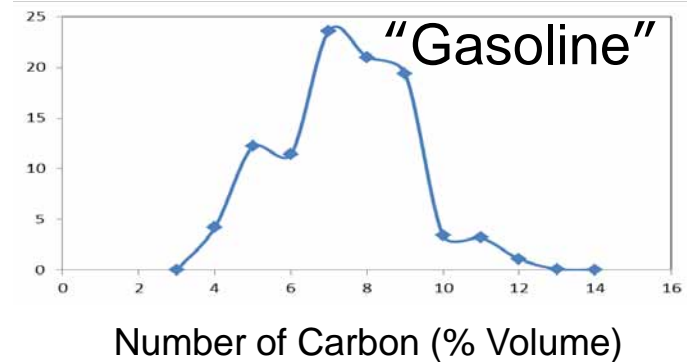




# Ethanol Derived Fuel Blendstocks

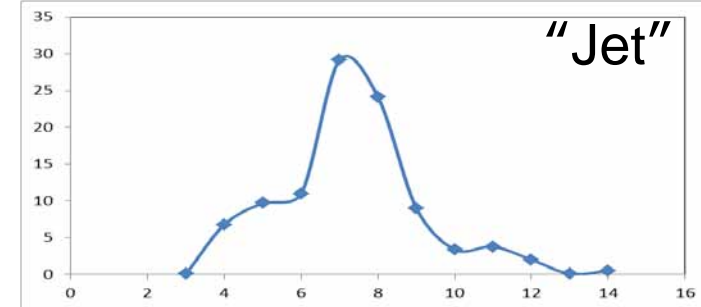
- Gasoline blendstocks

- Total Calculated Research Octane # (RON) = 105.7
- Total Calculated Motor Octane # (MON) = 90.6
- Average MW = 96
- 60% aromatics

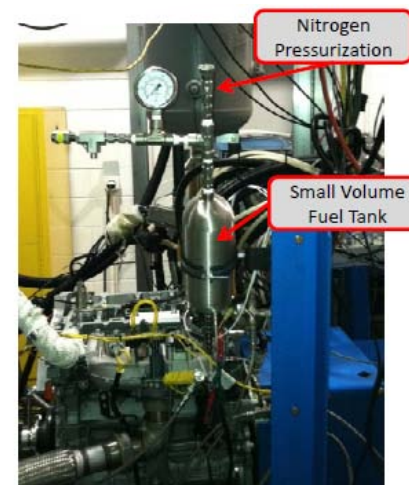


- Diesel/Jet blendstocks

- Total Calculated RON = 112.7
- Total Calculated MON = 95.5
- Average MW = 95
- 75% aromatics



- Gasoline blendstock tested in internal combustion engine with comparable performance



Small volume (<250 mL) test in Sturman variable actuation engine

# Critical Success Factors

- Technical, economic, and business factors
  - Low cost durable catalyst that converts alcohol stream(s) to blendstock at moderate conditions
  - More ethanol capacity than necessary to meet the blend needs
- Commercial viability
  - U.S. Patent Applications
    - Zeolitic catalytic conversion of alcohols to hydrocarbons
    - Catalytic conversion of alcohols to hydrocarbons with low benzene content
    - Catalytic conversion of alcohols having at least three carbon atoms to hydrocarbon blendstock
  - Technology licensed to Vertimass, LLC

# Progress Against Current Milestones

- Milestones

- Obtain experimental data for mass balance and heat of combustion of the produced blendstocks for energy balance data [complete].
- Update TEA based on FY14 data and energetics [in progress].
  - Prior preliminary NREL TEA showed \$3-4/gal gasoline equivalent from cellulosic ethanol (based on 2011 NREL TEA from corn stover ethanol)
  - Updated preliminary TEA ~\$5/gal from cellulosic ethanol
    - Updated all the financial assumptions to be consistent with all ongoing design report models, including higher feedstock cost, low process efficiency, current light co-product values, etc.
- Reduce C2 (ethylene) to ~1% or less and C2+C3 to less than 5% at the laboratory scale. Confirm that coke production is a negligible % [in progress].
- Reduce BTX to below 15% with benzene below 0.68% (EPA regulatory requirement) and overall aromatics to ~40% [in progress].
- Provide process data (energy and mass balance, reaction temperature and space velocity and product analysis) for detailed TEA [in progress].

# Relevance

- The project accomplishments show a chemical pathway (catalytic process) to convert hydrolysis product (fermentation stream with ethanol) to hydrocarbon blendstock that can be fractionally collected and mixed with gasoline, jet-fuel, or diesel.
  - Blendstock suitable for mixing with petroleum derived fuel in any ratio
  - No benzene in product stream (EPA regulates to 0.68%)
- The catalyst unit can be retrofitted to existing refineries or built into new ones

# Future Work

- Goals to finish project (by 9/2016) are
  - Decrease less desirable lights to improve fuel quality
  - Control aromatics to improve fuel quality
  - Update TEA parameters
  - Complete publications
  - Transfer results to Vertimass for accelerated commercialization

# Summary

- Approach: Our technical approach employs mechanistic studies to direct catalyst development for ethanol conversion to hydrocarbon blendstock
- Technical Accomplishments: We have shown that ethanol can be converted to hydrocarbon blend-stock at 350°C and atmospheric pressure. The catalyst is durable
- Relevance: Production of hydrocarbon blend-stock from biomass
- Critical success factors: Beyond go/no-go point
- Future work: Project completion
- Technology Transfer: Technology licensed to Vertimass, LLC



# Additional Slides

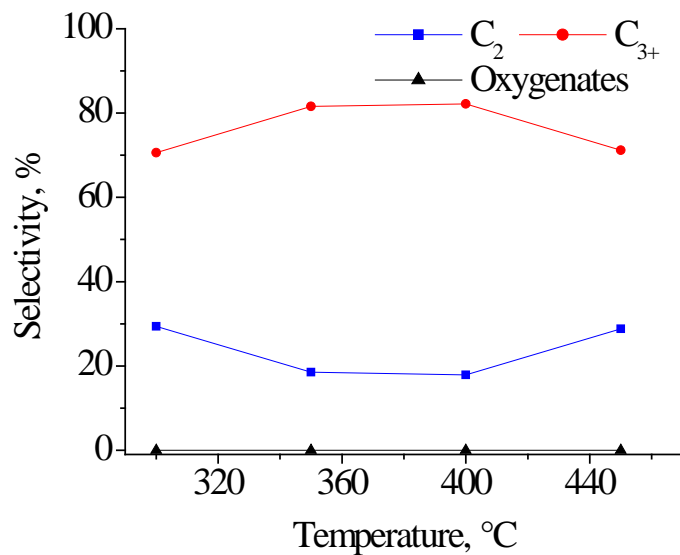
# Patents and Commercialization

- Technology Licensed to Vertimass, LLC on March 6, 2014
- Patents
  - Based on BETO work
    - C. K. Narula, B. H. Davison, and M. Keller, Zeolite catalytic conversion of alcohols to hydrocarbons, U.S. Patent Application 13/787112, March 6, 2013.
    - C. K. Narula, B. H. Davison, and M. Keller, Catalytic conversion of Alcohols to hydrocarbons with Low benzene content, U.S. Patent Application 20140322781, October 30, 2014.
    - C. K. Narula and B. H. Davison, Catalytic conversion of alcohols having at least three carbon atoms to hydrocarbon blend-stock, U.S. Patent Application 20150011813, January 8, 2015.
  - Other Patents
    - C. K. Narula and X. Yang, Zeolite based SCR catalysts and their use in diesel engine emission treatment, U.S. Patent Application 12/855.794, allowed on November 14, 2014.
    - C. K. Narula and X. Yang, Hydrothermally stable low-temperature NOx reduction NH3-SCR catalyst, U.S. Patent Application 13/404,071, allowed on November 19, 2014.

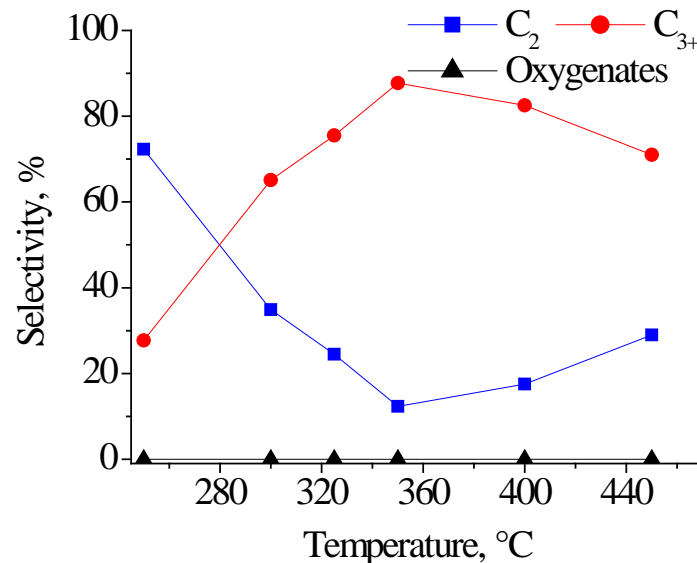
# Publications and Presentations

- R. Geiger, B. H. Davison, J. Szybist, M. Keller, and C. K. Narula, "Direct Catalytic Conversion of Ethanol Stream into Fuel," ACS Spring Meeting, San Diego, March 25, 2012.
- R. Geiger, E. Casbeer, B. H. Davison, J. Szybist, M. Keller, and C. K. Narula, "Direct Catalytic Conversion of Ethanol Stream into Blend-Stock Fuel," ACS Fall Meeting, Philadelphia, 2012 (abstract published, presentation not made due to travel restrictions).
- R. Geiger, E. Casbeer, B. H. Davison, J. Szybist, M. Keller, and C. K. Narula, "Direct Catalytic Conversion of Ethanol Stream into Blend-Stock Fuel," ACS Spring Meeting, New Orleans, 2013.
- C. K. Narula, B. H. Davison - BETO merit review – May 20-22, 2013, Alexandria, Virginia.
- R. Geiger, E. Casbeer, B. H. Davison, J. Szybist, M. Keller, C. K. Narula, "Hydrocarbon Blend-Stock from Catalytic Conversion of Biomass Derived Ethanol," North American Catalysis Society Meeting, Louisville, Kentucky, 2013.
- E. Casbeer, J. Szybist, C. Kinchin, M. Keller, Davison, B.H., and C. K. Narula, "Direct Catalytic Conversion of Aqueous Ethanol Streams into Hydrocarbon Blendstock," 35th Symposium on Biotechnology for Fuels and Chemicals, April 29-May 2, 2013, Portland, Oregon.
- E. M. Casbeer, A. W. Lepore, B. H. Davison, and C. K. Narula, "Direct Catalytic Conversion of Alcohols Stream into Hydrocarbon Blend-Stock," American Chemical Society International Fall Meeting, San Francisco, August 10-14, 2014.
- E. Casbeer, R. A. Geiger, B. H. Davison, J. P. Szybist, M. Keller, and C. K. Narula, "Hydrocarbon-Pool Route to Conversion of Biomass Derived Ethanol to Hydrocarbon Blend-Stock," American Chemical Society International Fall Meeting, Indianapolis, September 8-12, 2014.

# Ethanol Conversion over H-ZSM-5 and V-ZSM-5



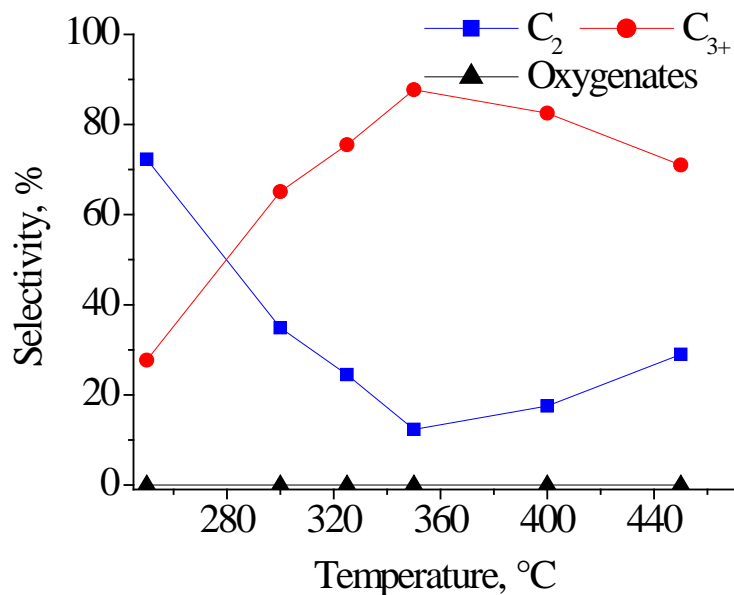
**H-ZSM-5 at WHSV 1.6h-1**



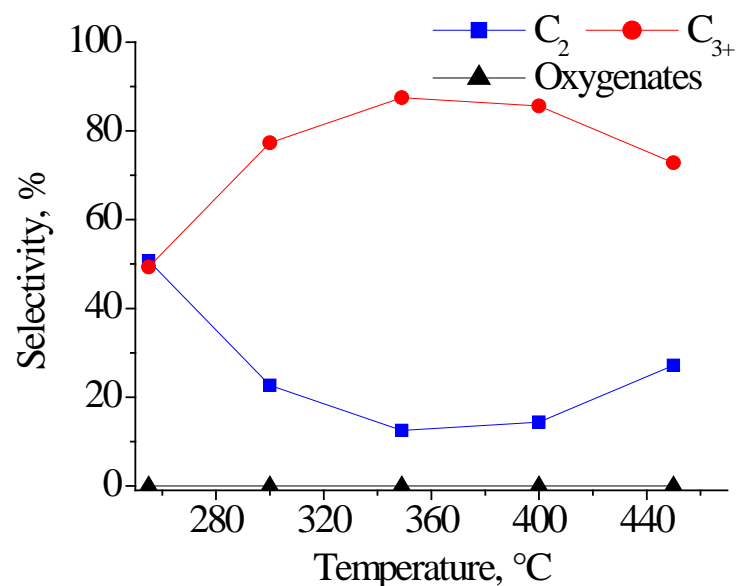
**V-ZSM-5 at WHSV**

- The plots show ethanol conversion to C<sub>3+</sub> hydrocarbons and ethylene (C<sub>2</sub>) as a function of temperature. Water yields are omitted for simplicity.
  - Ethanol conversion is stoichiometric.
  - Catalyst regenerates in air under 450°C

# Heterobimetallic Zeolites



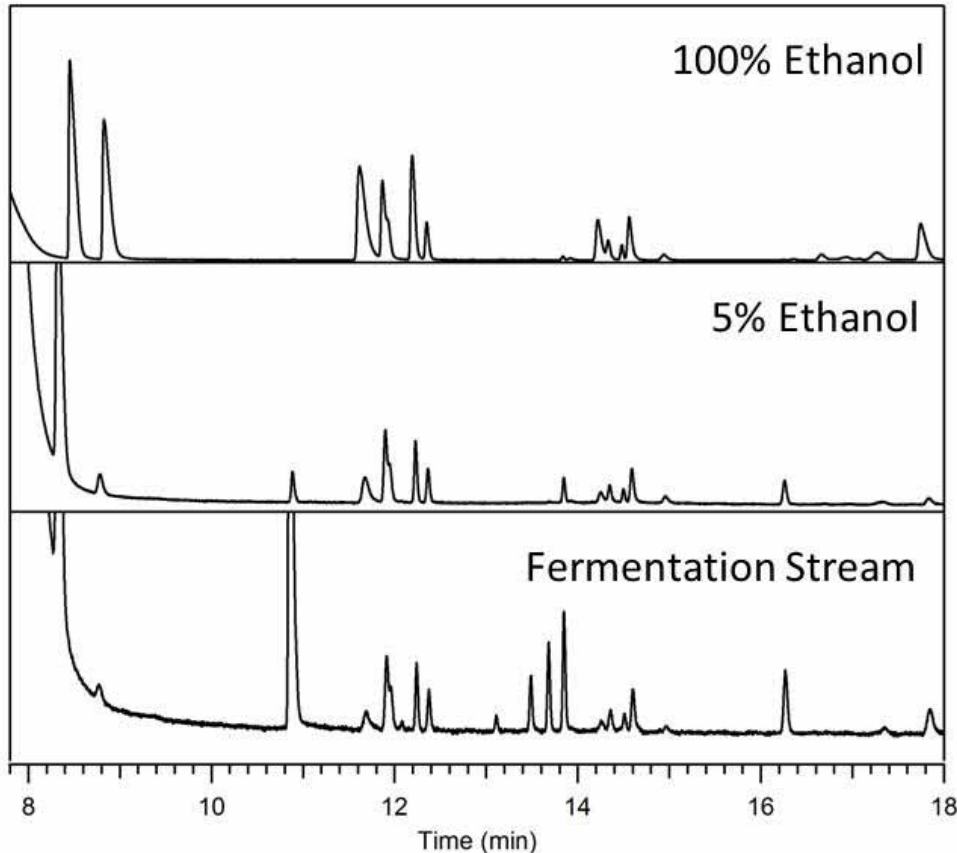
V-ZSM-5 at WHSV 1.6



InV-ZSM-5 at WHSV

- InV-ZSM-5 shows lower C<sub>2</sub> at low temperature: 250-300°C
- Similar C<sub>2</sub> selectivity above 350°C
- InV-ZSM-5 exhibits a broader temperature window for C<sub>3+</sub>

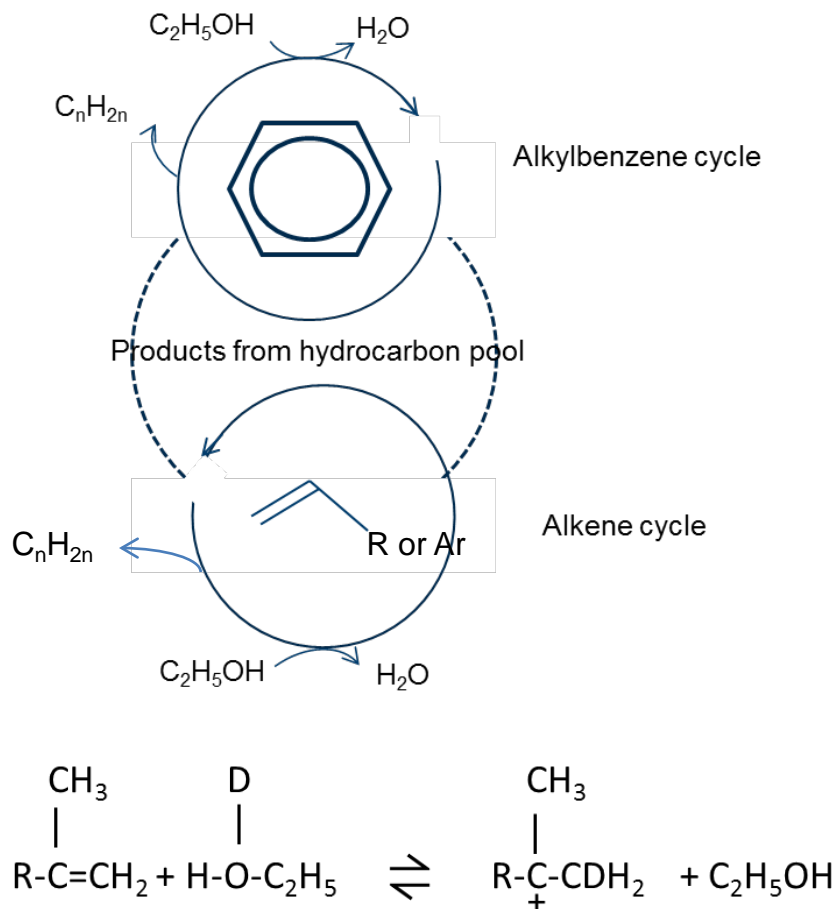
# Simulated Fermentation Stream - Products Are Very Similar



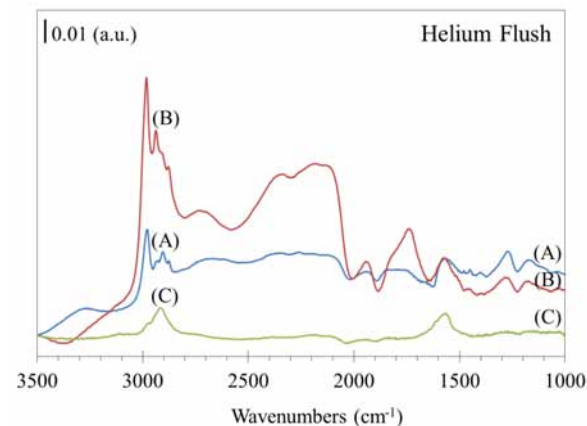
- Partial GC Trace of Product Stream
- Simulated Fermentation Stream
  - Microorganism: Yeast *Saccharomyces cerevisiae*
  - Medium: Yeast extract + Peptone + Dextrose
  - ~ 4.7% Ethanol



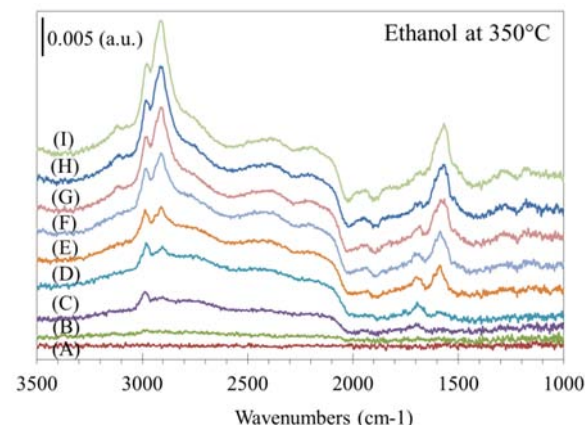
# Mechanism is Hydrocarbon Pool Mechanism, Not Conventional Ethylene Pathway



Scheme 2.  $C_2H_5OD$  addition across double bond

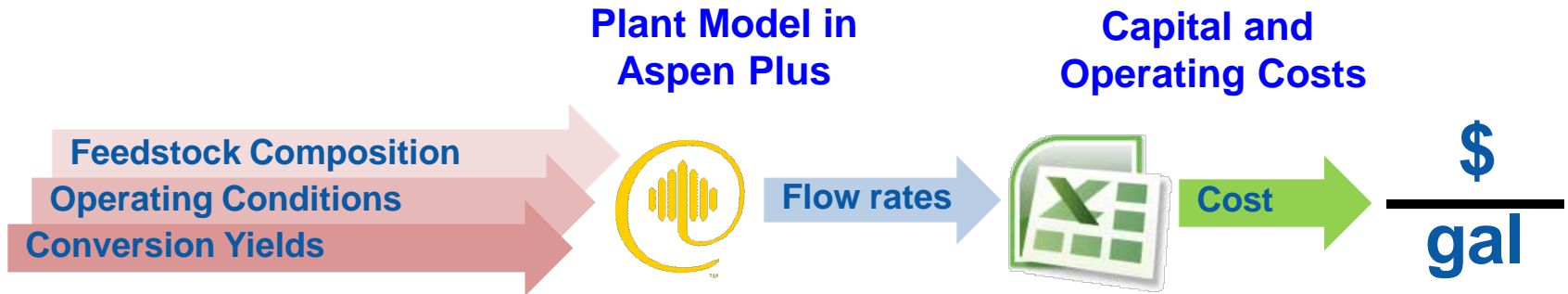


A, B, and C are Diffuse Reflectance Infrared Fourier Transform Spectroscopy of catalyst surface after exposure to ethanol at 25, 200, and 350°C.



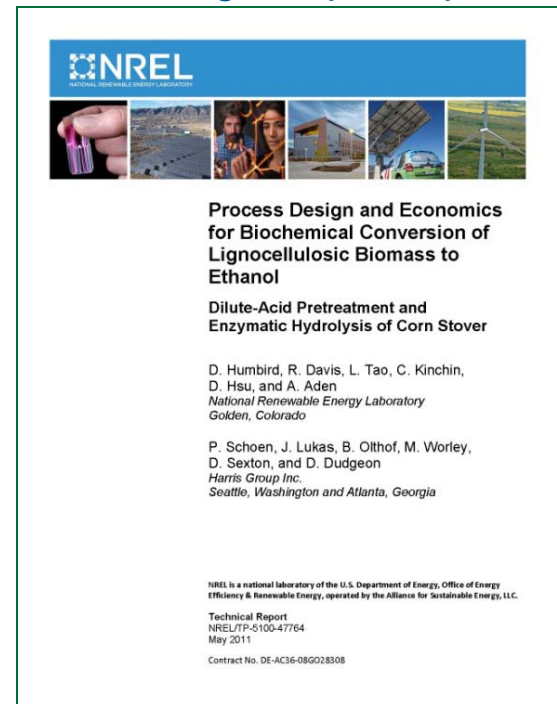
Changes in DRIFTS as a function of ethanol exposure time (A) no exposure (B) 0.1 min; (C) 0.2 min; (D) 0.5 min; (E) 1.3 min; (F) 2.9 min; (G) 5.0 min; (H) 6.9 min; (I) 10.0 min.

# Technoeconomic Model Introduction



- Process model in Aspen Plus based on NREL research for biomass to ethanol steps (2011 Biochemical Design Report Update), ORNL research for ethanol to hydrocarbon step
- Assumes  $n^{\text{th}}$ -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 2012

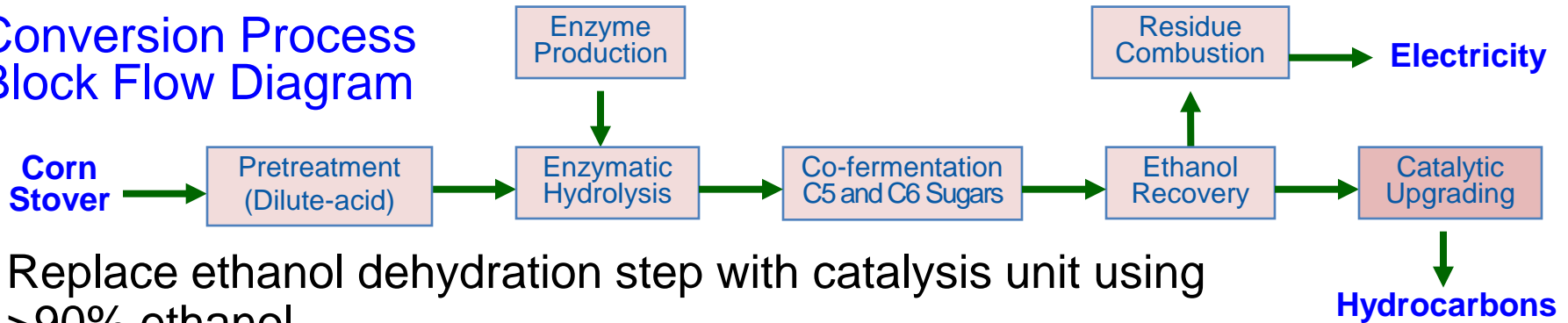
## 2011 Design Report Update



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

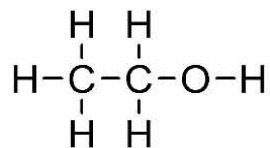
# Modeling Assumptions

## Conversion Process Block Flow Diagram

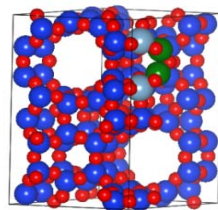


- Replace ethanol dehydration step with catalysis unit using >90% ethanol
- Plant size: 2,200 dry U.S. ton/day corn stover
- Incoming moisture: 20%
- Ethanol Yield: 79.0 gal/dry U.S. ton feedstock
- Feedstock cost: \$58.50/dry ton
- Internal Rate of Return: 10%
- Equity Percent of Total Investment: 40%, 8% interest on difference
- Upgrading of Ethanol Yields (mole %): 40.0% water, 15.6% ethylene, 44.4% hydrocarbon product
- Upgrading reactor conditions: 350°C, LHSV of 1.17 hr<sup>-1</sup>
- Separate C4- by distillation, combust for heating value
- Techno-economic analysis is on-going. Results will be available soon.

# Ethanol Upgrading Into Fuel Blendstocks Bypasses the Ethanol Blendwall

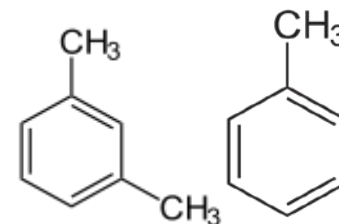


Ethanol or  
fermentation  
stream



Low-cost metal-exchanged zeolite catalyst

Aromatic and Aliphatic HCs typical ) of blendstock constituents (C<sub>4</sub>-C<sub>12</sub>) with water and trace ethylene byproducts



- Quantitative conversion of ethanol to hydrocarbons with liquid fuel yield of ~54-55% at 310°C. Ethylene and water byproducts ~6-7% and ~39%, respectively.
- Calculated octane number of products ~95
- Engine experiments at ORNL, designed for 250ml fuel, show combustion similar to gasoline
- No added hydrogen
- Possible new hydrocarbon pool mechanism
- Now TRL 3-4
- Possible show stoppers - none
- Catalyst durability at par with methanol-to-gasoline catalysts for 200h test
- Catalyst de-coking at 450°C.

Group	% Volume
Paraffins	3.855
I-Paraffins	9.588
Olefins	5.371
Naphthalenes	1.988
Aromatics	79.198
Oxygenates	0.00
Unidentified	4.203