

Direct Catalytic Upgrading of Current Dilute Alcohol Fermentation Streams to Hydrocarbons for Fungible Fuels

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Technology Area Review: Biochemical Conversion
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(This presentation does not contain any proprietary, confidential, or otherwise restricted information.)

Goal

- The program objective is take the ethanol upgrading technology from TRL 2 to TRL 3 and beyond during the course of investigation.
- Our initial success has led to discovery of catalyst that operates at 350°C and atmospheric pressure. Nevertheless, the side reactions produce coke which impedes the primary reaction of ethanol to C3+ hydrocarbons. Periodic decoking is required to remove coke.
 - We plan to focus on improving the durability of the catalyst for use with a bioethanol at any stage of purification.
 - The work will also allow us to develop detailed mass balance and energy balance data that are needed for detailed technoeconomic analysis.
 - We will also carry out fractional collection of blend-stock and get blend-stocks tested on gasoline, diesel, and jet engines.

Quad Chart Overview

Timeline

- Project start date: October 1, 2011
- Project end date: September 30, 2015
- Percent complete: 30%

Budget

- Funding for FY12: 150,000
- Funding for FY13: 400,000
- Years the project has been funded / average annual funding.
2/275,000

Barriers

- Overcoming blend-wall for biomass derived fuel
- Techno-economically feasible process
- Technology uses existing infrastructure for manufacturing and distribution.

Partners

- Multiple inquiries and follow-up discussions, but developing commercialization plans
- Ongoing collaboration with NREL for technoeconomic analysis
 - Christopher Kinchin
 - Ling Tao

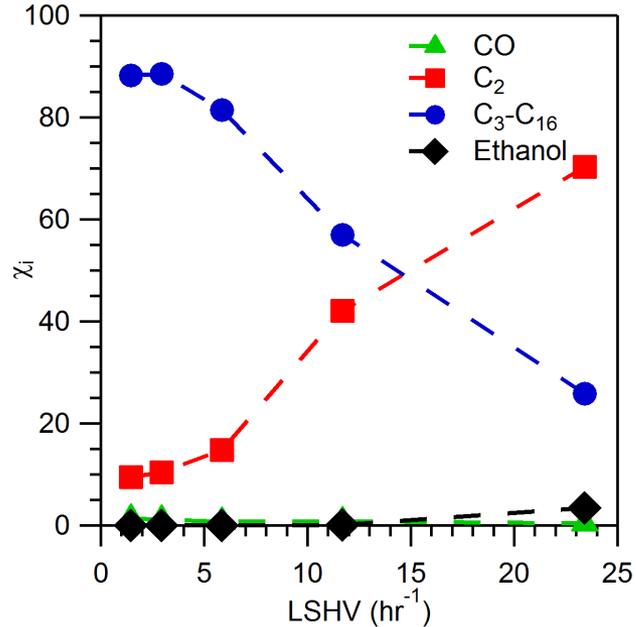
Overview

- 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% (or 15% for vehicles of model year 2001 or beyond). Use of ethanol beyond this blend wall requires Flex-Fuel Vehicles which have been available for 25+ years but have a low market penetration
- Catalytic conversion of ethanol to hydrocarbon blend-stock overcomes the blend wall
- Our objective is to find a durable catalyst that can convert ethanol in fermentation stream at any stage of purification to hydrocarbon blend-stock under moderate conditions. This will lead to blend-stock cost competitive with petroleum derived fuel.

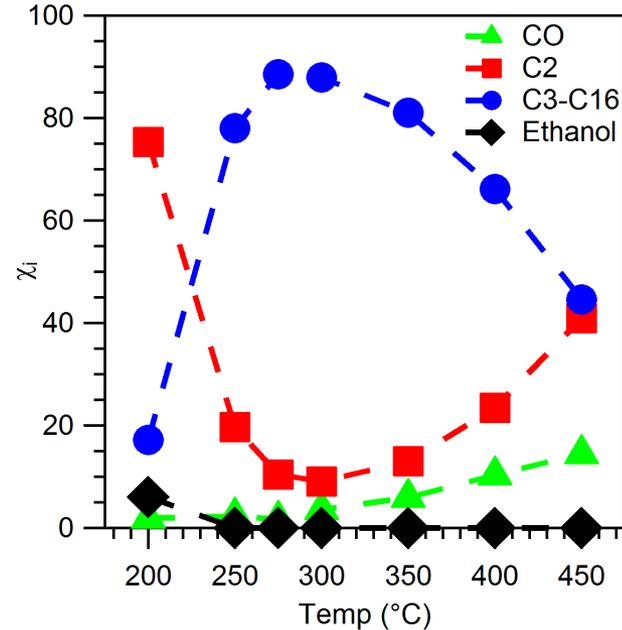
Approach

- Our technical approach employs mechanistic studies to direct catalyst development for ethanol conversion to hydrocarbon blend-stock
- The project is organized under following tasks and subtasks
 - TASK 1. Synthesis, characterization, and testing of metal-exchanged zeolites as catalysts for ethanol (pure alcohol) upgrading
 - Subtask 1A. Conversion of ethanol in fermentation streams at various stages of purification
 - Subtask 1B. Fractional collection of blend-stock for gasoline, diesel, and jet fuels
 - Task 2: Technoeconomic Analysis (w/ NREL)
- Our major “go-no go” decision point was based on catalyst durability

Ethanol Conversion



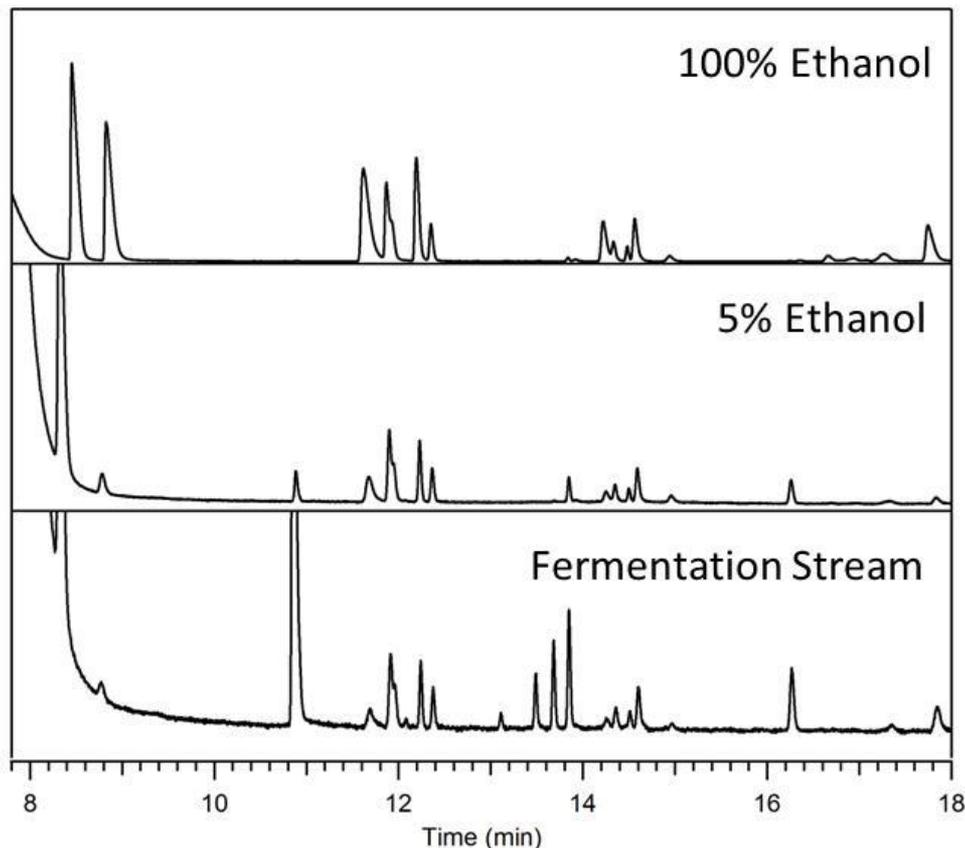
Constant Temperature 350°C



Constant LHSV of 2.93 h^{-1}

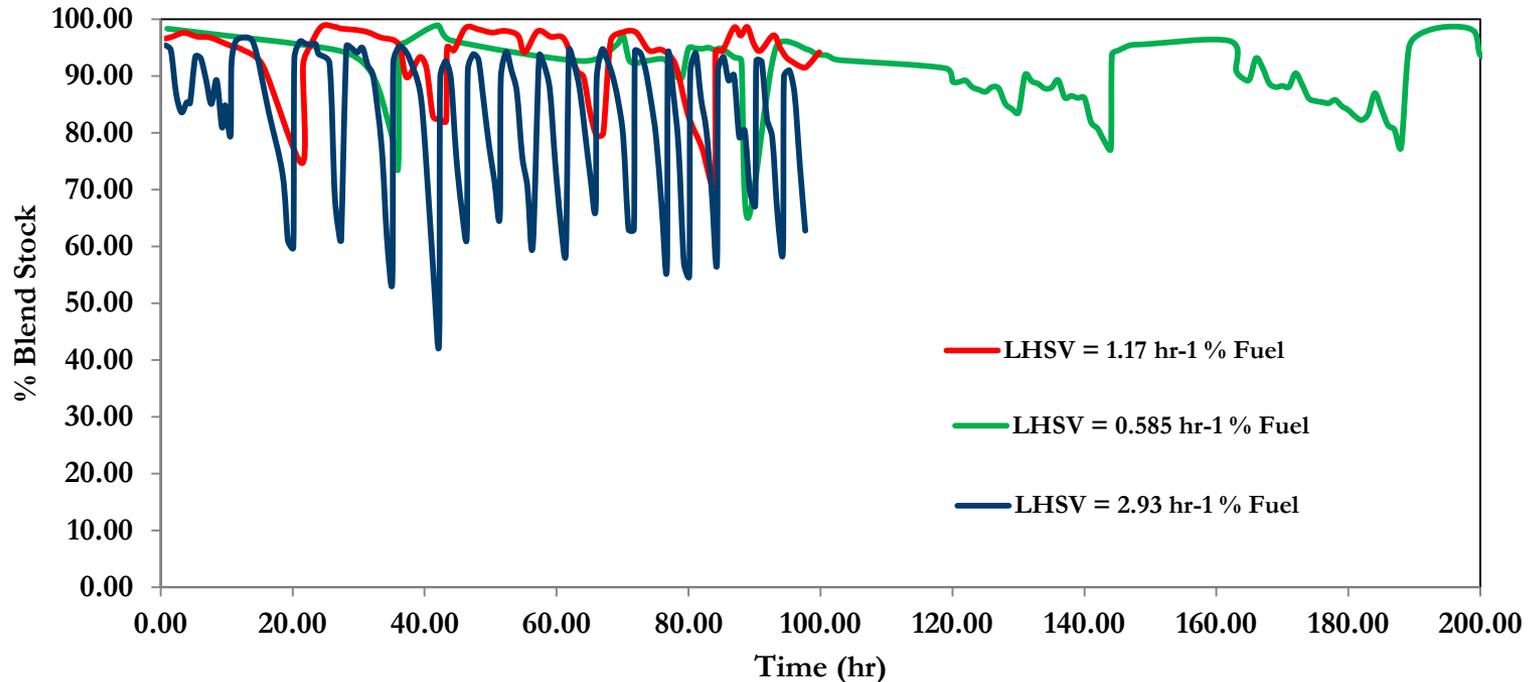
- The plots show ethanol conversion to hydrocarbons and ethylene as a function of Liquid Hourly Space Velocity (LHSV) and Temperature. Water yields are omitted for simplicity
 - Ethanol conversion is stoichiometric.
 - The preferred initial condition is 350°C at LHSV of 1.2 h^{-1}
 - Catalyst regenerates in air under 450°C

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

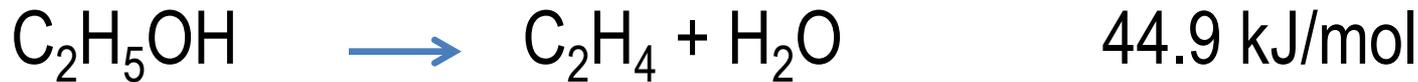
Catalyst Durability



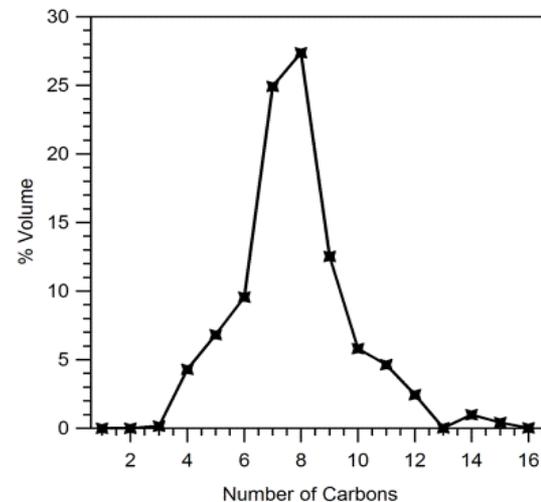
- Catalyst was operated at 350°C at a specified LHSV till C2+ formation started to fall
- Catalyst was decoked by heating at 450°C and operation restarted
 - 200h at LHSV of 0.59 h⁻¹
 - 100h at LHSV of 1.17 and 2.93 h⁻¹

Mechanism

- In order to get accurate data on the energy balance, the knowledge of ethanol conversion pathway is essential
 - The consensus in literature reports is that ethanol first converts to ethylene

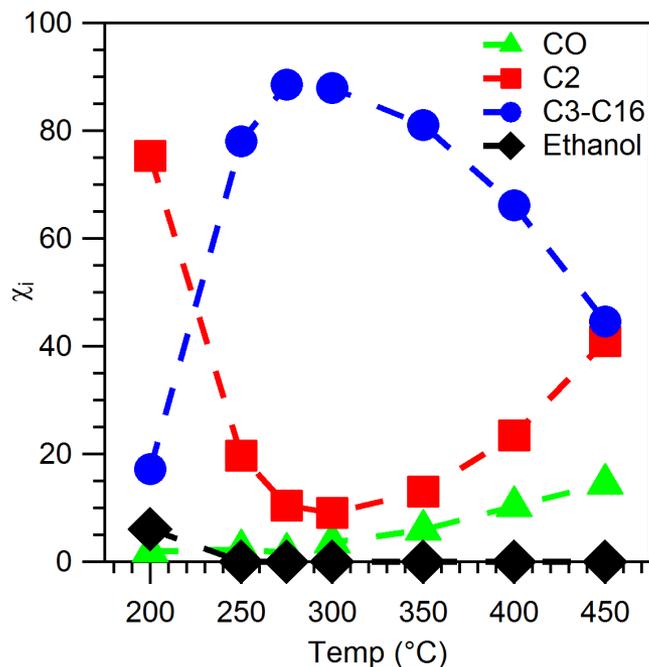


Product distribution does not show bias towards even carbon hydrocarbons!

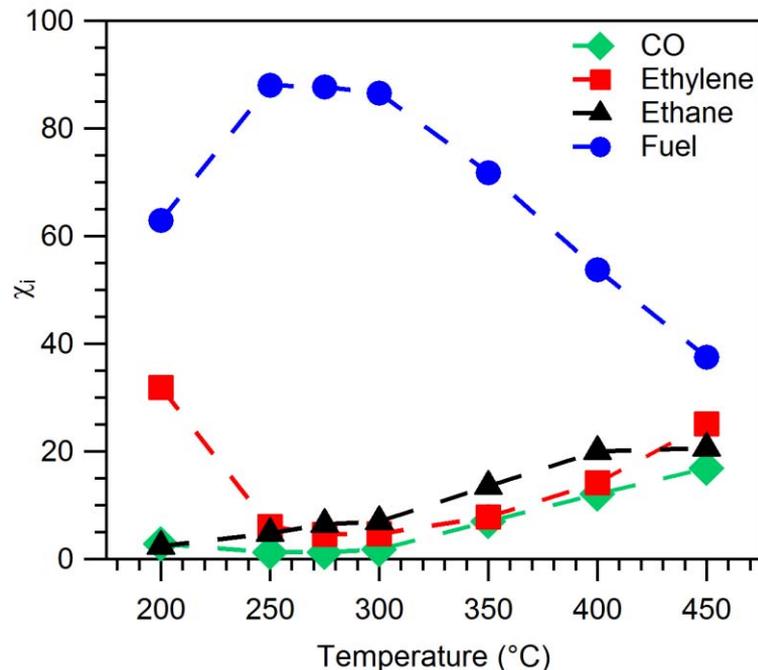


Mechanism – Comparison with ethylene conversion

- Ethanol and ethylene conversion to hydrocarbons as a function of temperature at LHSV of 2.93 h^{-1} (for ethylene, SV of 2241 h^{-1} is equivalent to ethanol LHSV of 2.93 h^{-1})
- Ethylene conversion less efficient than ethanol



Ethanol Conversion



Ethylene Conversion

Mechanism – Experiments with Deuterated Ethanol

- C₂H₅OD Experiment
 - Deuterium incorporation



Scheme 1: Hydrocarbon from ethanol via ethylene

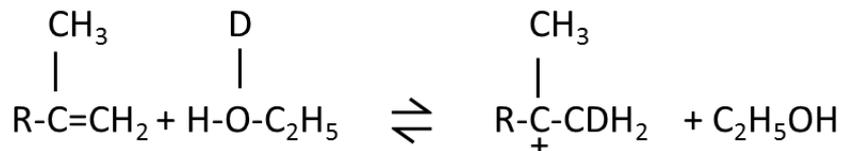
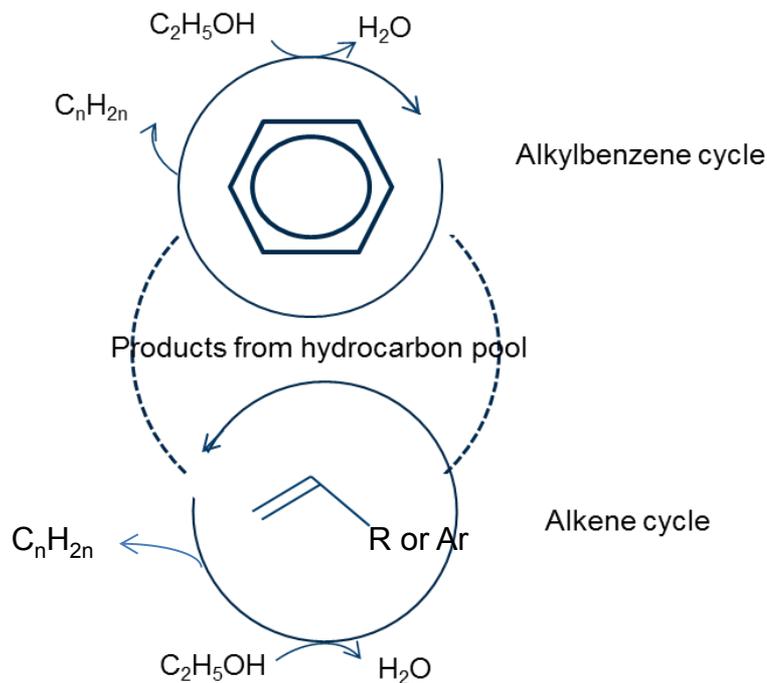
- D₂O Experiments
 - Ethanol (70%) + D₂O (30%)
 - Deuterium incorporation in all hydrocarbons except ethylene
 - Ethylene (70%) + D₂O (30%)
 - No deuterium incorporation

Rules out ethylene via the conventional mechanism

Mechanism – Experiments with ^{13}C labeled Ethanol

- Reaction of $^{13}\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3^{13}\text{CH}_2\text{OH}$ over catalyst at 350°C .
- Scrambling of ^{13}C in product stream indicates hydrocarbon pool mechanism
- Pathway via ethylene not supported by product stream
 - Ethylbenzene contains four ^{13}C regardless of precursor as expected
 - Toluene contains four ^{13}C regardless of precursor
 - Should contain three ^{13}C from $^{13}\text{CH}_3\text{CH}_2\text{OH}$
 - Should contain four ^{13}C from $\text{CH}_3^{13}\text{CH}_2\text{OH}$

Mechanism – Hydrocarbon Pool Mechanism, a Likely Pathway



Scheme 2. C_2H_5OD addition across double bond

- Methanol Conversion

- 1,3-dimethylcyclopentadienyl cation
- 1,1,2,4,6-pentamethylbenzenium cation

MTG Mechanism: Speybroeck et al., ChemCatChem, 2011, 3, 208

- Ethanol Conversion

- NMR evidence

- Surface ethoxy at 20°C
- Oligomeric alkoxy at 250°C

- UV-Vis

- Polyaromatics and unsaturated carbenium cations, such as, dienylic, trienylic carbenium or alkyl-substituted benzenium cations

Hunger et al., ChemPhysChem, 2005, 6, 1467

Mechanism – Alkylation of Aryl Compounds

- The hydrocarbon pool mechanism suggests
 - Aromatic ring alkylation in mono-substituted benzenes
 - Alkyl groups on benzene are ortho, para-directing
 - Side chain alkylation in tri- or higher substituted benzenes
 - Steric hindrance
 - ortho, para-positions occupied
- Experiments with a mixture of ethanol with
 - Mono-substituted benzenes – ethylbenzene, cumene, toluene – Aromatic ring alkylation
 - Tri-substituted benzene – 1,2,4-trimethylbenzene – side chain alkylation

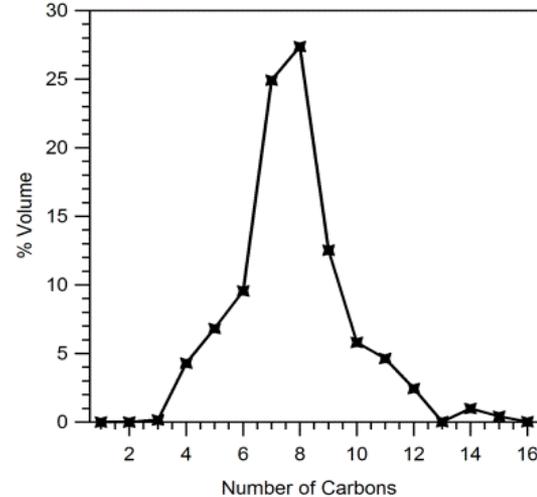
Better energy balance – No endothermic ethylene formation

Analysis of Fuel Product

- Analysis at SGS North America, 1201 W 8th Street, Deer Park, TX
 - Boiling Range of ~ 30°C to 270°C
 - Composition by % Vol of Group
 - Total Calculated RON = 111.51
 - Total Calculated MON = 94.87

Calculated	Total
Avg MW	99.98
Avg SG	0.842
Avg API @ 15.6 °C	38.54
RVP	3.813
Tot H	9.873
C/H	9.087
E200	9.162
E300	74.148

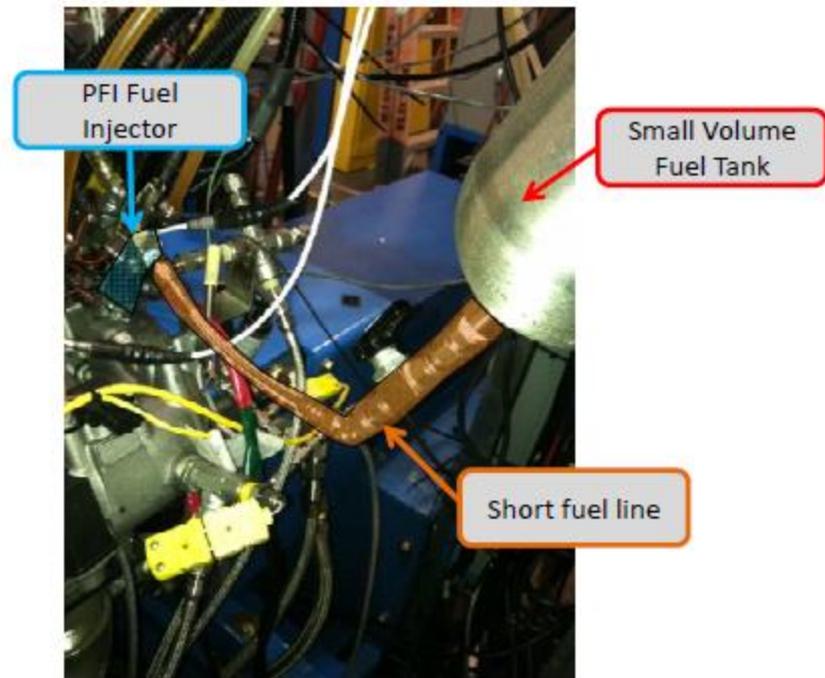
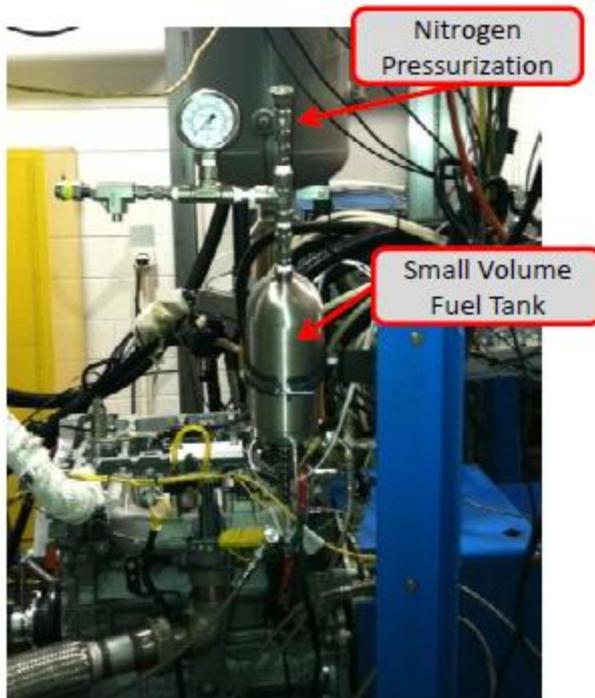
Fuel Properties



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

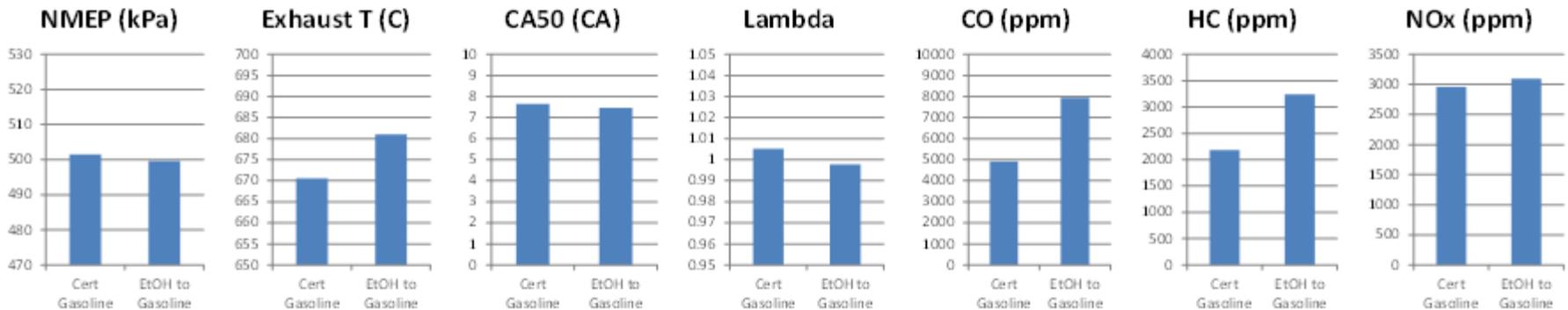
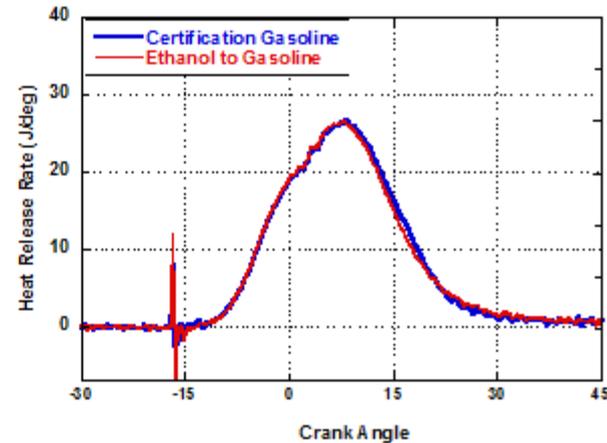
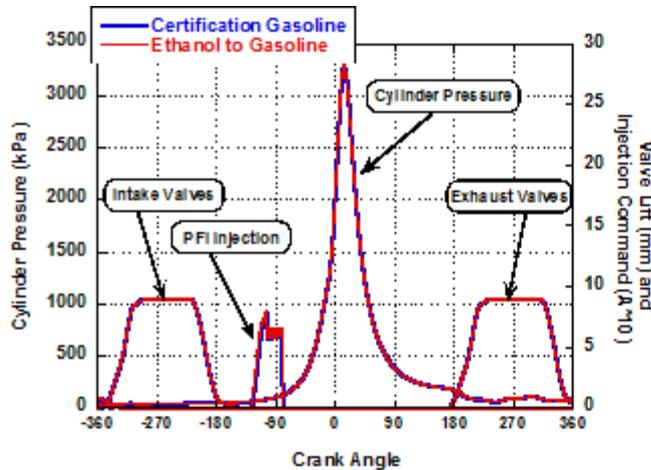
Engine Testing

- Sturman variable valve actuation engine which can run at a low fuel quantity
 - Ported Fuel Injection (rail pressure 5 bar)
 - Engine was warmed-up using the gasoline direct injection fueling system so that none of the sample fuel was consumed



Engine Testing

- Experimental demonstration shows comparable engine performance to certification gasoline with PFI fueling at 2000 rpm 5 bar net mean effective pressure



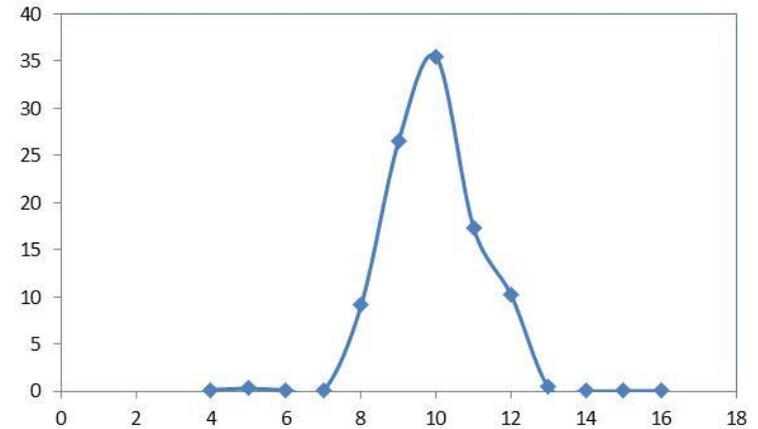
* Small quantity of fuel (250 mL) prevented lambda from being fine-tuned, resulting in predictable increases in CO and HC emissions for ethanol to gasoline fuel

Jet Fuel/Diesel Blend Stock

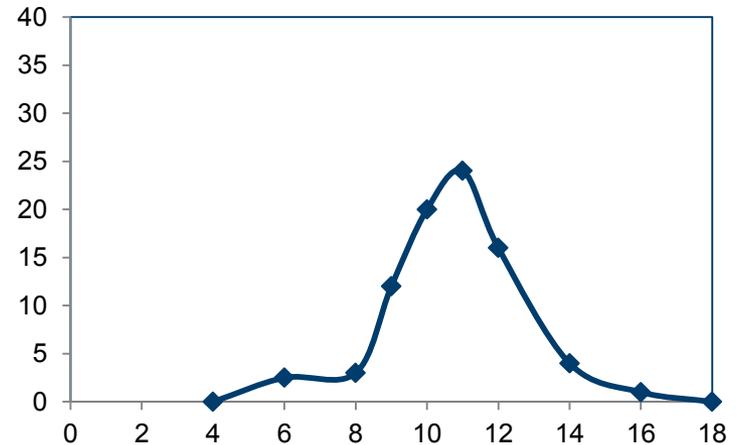
- Analysis at SGS North America, 1201 W 8th Street, Deer Park, TX
 - Boiling Range of ~ 160°C to 300°C
 - Composition by % Vol of Group
 - Total Calculated RON = 94.2
 - Total Calculated MON = 95.6

Calculated	Total
Avg MW	129.97
Avg SG	0.88
Avg API @ 15.6 °C	30.1
RVP	0.43
Tot H	9.4
C/H	9.63
E200	0
E300	4.59

Fuel Properties

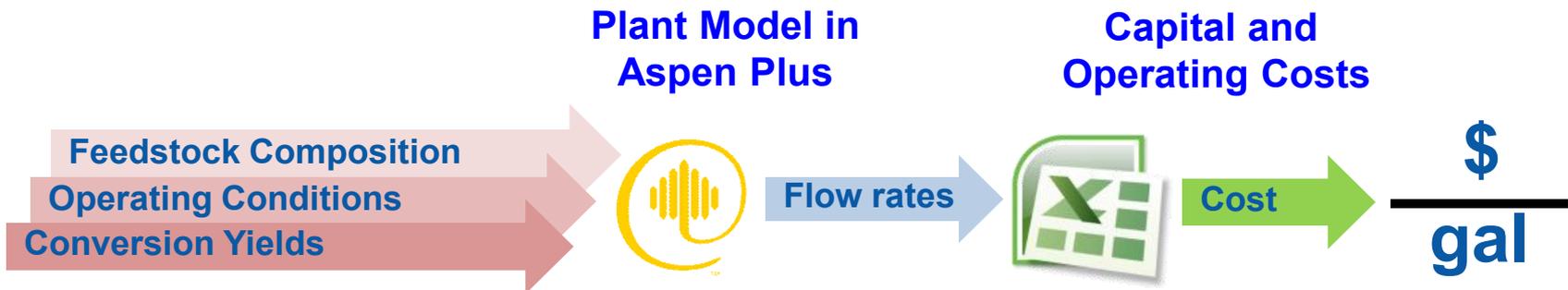


Blend Stock



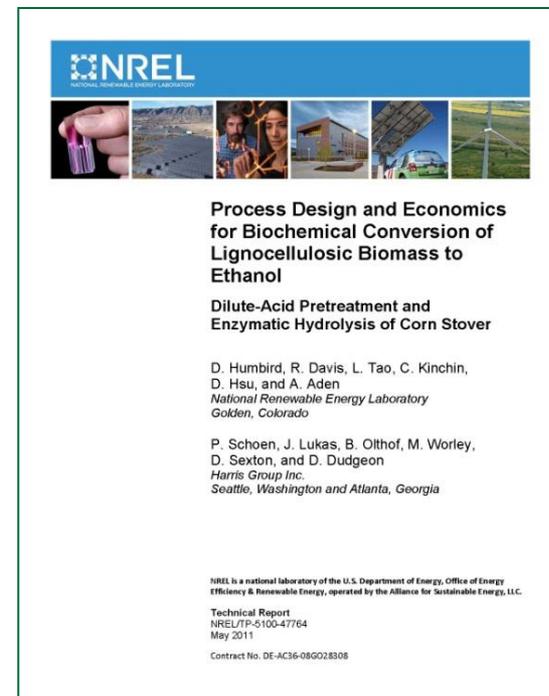
Typical Jet Fuel

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^{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

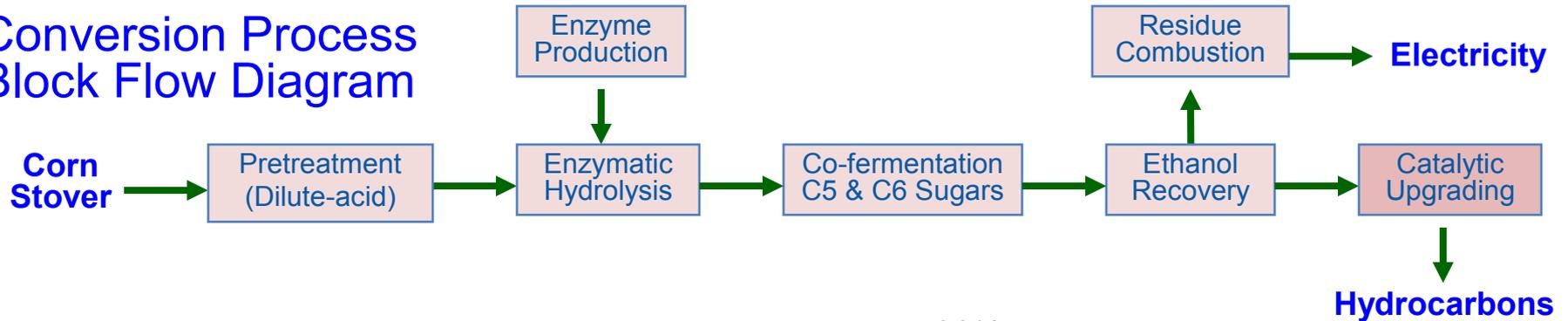
2011 Design Report Update



<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 US 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⁻¹
- Separate C4- by distillation, combust for heating value
- Techno-economic analysis is on-going. Results will be available soon.

Progress against milestones

- Milestones
 - Perform durability tests for 100h equivalent. [Completed]
 - Provide improved mass and energy data to enable techno-economic assessment [in progress]
 - Perform durability test of 200h equivalent and gather >1 L of blendstocks [Completed]
 - Perform and report on engine tests of blendstocks [initial tests complete]
- Fermentation stream testing
 - Initiated with simulated fermentation streams
 - Planned for corn starch ethanol and cellulosic ethanol

Relevance

- The project accomplishments show a Chemical Pathway (catalytic process) to convert hydrolysis product (fermentation stream with ethanol) to hydrocarbon blend-stock that can be fractionally collected and mixed with gasoline, jet-fuel, or diesel.
 - Blend-stock 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

Critical Success Factors

- Technical, economic, and business factors
 - Low cost durable catalyst that converts alcohol stream(s) to blend-stock at moderate conditions
 - More ethanol being produced than necessary to meet the blend-wall needs
- Commercial viability will require scale-up
 - US Patent Applications
 - Zeolitic catalytic conversion of alcohols to hydrocarbons
 - Catalytic conversion of alcohols to hydrocarbons with low benzene content

Future Work

- Beyond “go/no go” point
- Testing conversion of fermentation streams
 - As produced
 - Distilled streams
- Testing of non-ethanol fermentation streams at various stages of purification

Summary

- Approach: Our technical approach employs mechanistic studies to direct catalyst development for ethanol conversion to hydrocarbon blend-stock
- 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: Fermentation streams containing ethanol and other alcohols
- Technology Transfer: Efforts to commercialize technology in progress

Additional Slides

Publications, Presentations, and Commercialization

- Geiger, R.; Davison, B.H.; Szybist, J; Keller, M.; Narula, C.K.; Direct Catalytic Conversion of Ethanol Stream into Fuel, ACS Spring Meeting, San Diego, March 25, 2012
- Geiger, R.; Casbeer, E.; Davison, B.H.; Szybist, J; Keller, M.; Narula, C.K.; Direct Catalytic Conversion of Ethanol Stream into Blend-Stock Fuel, ACS Fall Meeting, Philadelphia, 2012 (Abstract published, presentation not made due to travel restrictions)
- Geiger, R.; Casbeer, E.; Davison, B.H.; Szybist, J; Keller, M.; Narula, C.K.; Direct Catalytic Conversion of Ethanol Stream into Blend-Stock Fuel, ACS Spring Meeting, New Orleans, 2013
- Geiger, R.; Casbeer, E.; Davison, B.H.; Szybist, J; Keller, M.; Narula, C.K.; Hydrocarbon Blend-Stock from Catalytic Conversion of Biomass Derived Ethanol, North American Catalysis Society Meeting, Louisville, KY 2013 (accepted)
- Casbeer, E.; Szybist, J; C. Kinchin; Keller, M.; Davison, B.H.; Narula, C.K.; Direct Catalytic Conversion of Aqueous Ethanol Streams into Hydrocarbon Blendstock, 35th Symposium on Biotechnology for Fuels and Chemicals (April 29-May 2, 2013) at the Hilton Portland, Portland, OR.