Stretch Efficiency for Combustion Engines: Exploiting New Combustion Regimes

Project ID: ACE015

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DOE Management Team
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Project Overview

Barriers (MYPP 2011-2015, Section 2.4, Challenges and Barriers C.)

Lack of fundamental knowledge of advanced engine combustion regimes.

…inadequate understanding of the fundamentals of thermodynamic combustion losses

…inadequate capability to accurately simulate these processes

Budget

- FY11: $250k
- FY12: $250k
- FY13: $350k

Project Timeline

- ***Stretch Efficiency research program started at ORNL in 2005***
- ***Investigations have evolved based on comments from previous AMR reviews and will continue to evolve with emerging needs***

Industrial Partnerships and Collaboration

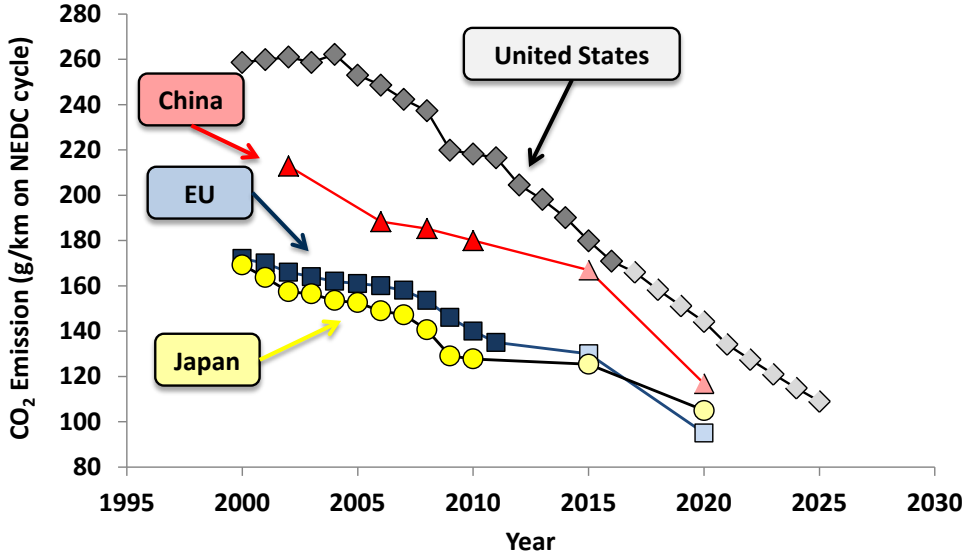
- ***AEC working group led by SNL***
  - ***Mechanism for industry feedback***
- ***SNL – Dick Steeper***
- ***Gas Technology Institute***
- ***Cummins***
- ***Sturman Industries***
- ***Drivven***

Universities

- ***Texas A&M University***
- ***University of Wisconsin***
- ***University of Michigan***
- ***Penn State University***

Objective: Increase Efficiency through Major Changes to Combustion Processes and Engine Architecture

Motivation: Legislation in U.S. and worldwide to reduce vehicle CO_2 emissions



Data from the International Council on Clean Transportation http://www.theicct.org/info-tools/global-passenger-vehicle-standards

Pursue thermodynamic strategies and implementation methods that could provide an increase in efficiency that is revolutionary rather than evolutionary

- Evolutionary technologies are defined as the current major paths forward, with room to grow (downsize and boost)
- This project is focusing on high risk, high reward technologies that could have a real world impact on longer-term timeframe (as defined by the 2010 Transportation Combustion Engine Efficiency Colloquium held at USCAR)

http://feerc.ornl.gov/pdfs/Stretch_Report_ORNL-TM2010-265_final.pdf

This Project has One Tracked Milestone for 2013

2013 Tracked Milestone

Quantify the product selectivity of in-cylinder non-catalytic fuel reforming for selected fuel components in the single-cylinder HVA engine after modifications are made to separate the combustion and recompression exhaust streams.

Status: Complete

Emphasis on Thermochemical Recuperation (TCR) Pathway to Higher Efficiency

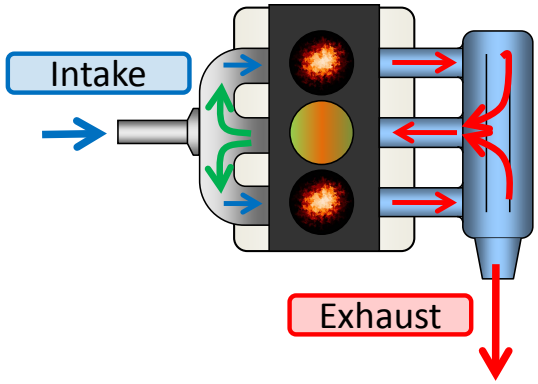
Motivation for Thermochemical Recuperation

- TCR is an attractive path to exhaust heat recovery that maintains a single work conversion device
- TCR through reforming theoretically increases lower heating value and exergy of fuel through endothermic reactions, driven by exhaust heat

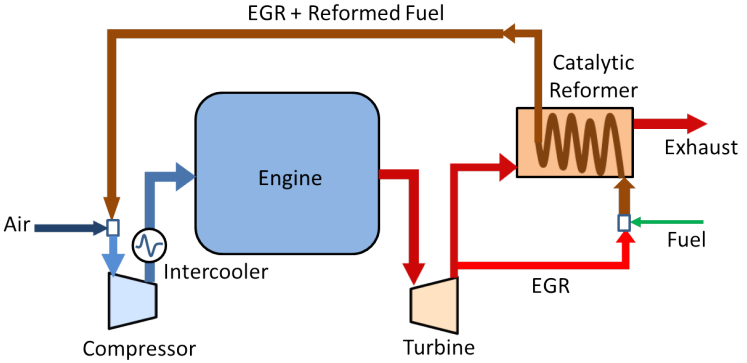
	Reforming Reaction	LHV Increase	Exergy Increase
Octane	$C_8H_{18} + 8H_2O \rightarrow 8CO + 17\ H_2$	25%	14%
Ethanol	$C_2H_5OH + H_2O \rightarrow 2\ CO + 4H_2$	24%	9%
Methanol	$CH_3OH \rightarrow CO + 2H_2$	20%	3%

*For information on why LHV increase is higher than exergy, See Szybist et al., *Energy & Fuels*, 2012 **26**; 2798-2810.

Pathway 1. In-cylinder Non-catalytic

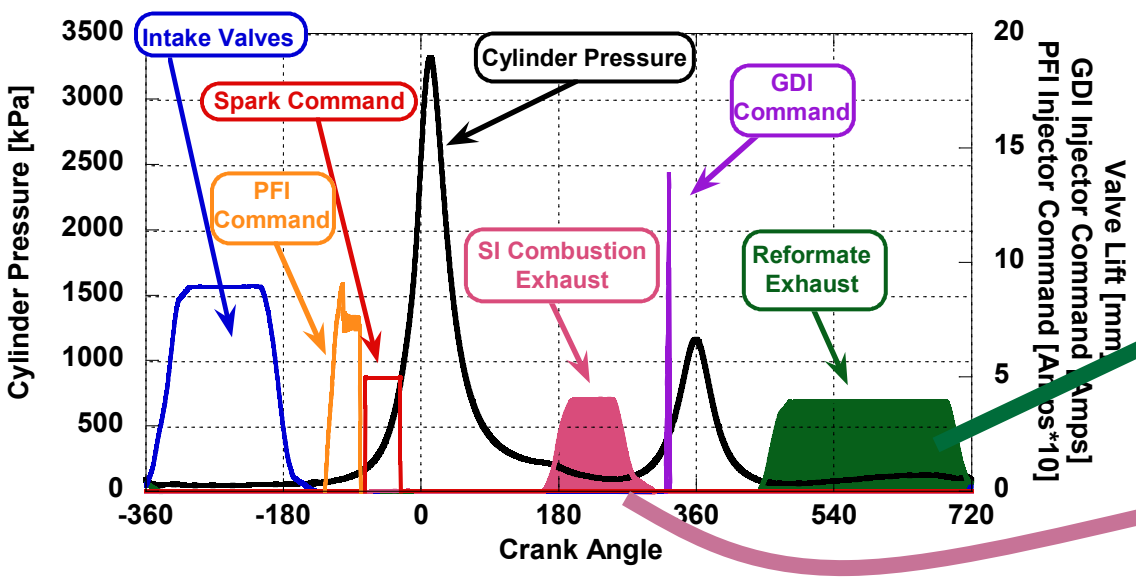


Pathway 2. Catalytic Reforming in EGR Loop

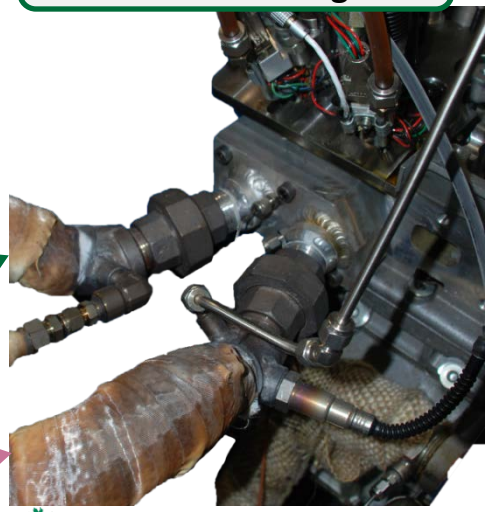


Pathway 1: Experimentally Determine Feasibility of Non-Catalytic TCR In-cylinder on Engine Timescales

- Flexible hydraulic valve actuation system on single-cylinder research engine used to enable unique engine cycles
  - Modified 2.0L GM Ecotec® engine
  - Wall-guided GDI fueling, aftermarket PFI fueling
  - Laboratory air handling (thermal management, external EGR)
  - Experiments conducted at compression ratio of 11.85:1
- Unique 6-stroke engine cycle used to investigate TCR on engine timescales
  - SI combustion event to setup a negative valve overlap (NVO) event
  - NVO products exhausted and chemically analyzed, modeled with various kinetic mechanisms
  - Findings applicable to NVO chemistry for HCCI and SA-HCCI



Divided Exhaust System on ORNL HVA Engine



Pathway 2: Identify Viable Catalyst Formulations for Application in EGR Loop TCR

- EGR TCR conditions vary from typical steam reforming applications
  - Low steam to carbon ratios
  - Residual exhaust oxygen, potential air exposure
  - Sulfur from fuels and lubricants
- Identifying catalysts with sufficient activity and durability is a first step toward implementation in future engine experiments
- GTI developed an EGR Loop TCR system with a Ni+Rh catalyst and evaluated it on a Cummins natural gas engine in a CEC funded project*
  - Reformer initially produced significant H_2
  - Catalyst rapidly deactivated during engine exhaust operation
  - Cause of deactivation unknown
- GTI supplied new and used TCR catalyst samples to ORNL
- We are characterizing the catalyst samples to identify and replicate the deactivation mechanism
  - Leverage GTI's prior development work
  - Identify formulation changes or operating strategies to improve durability

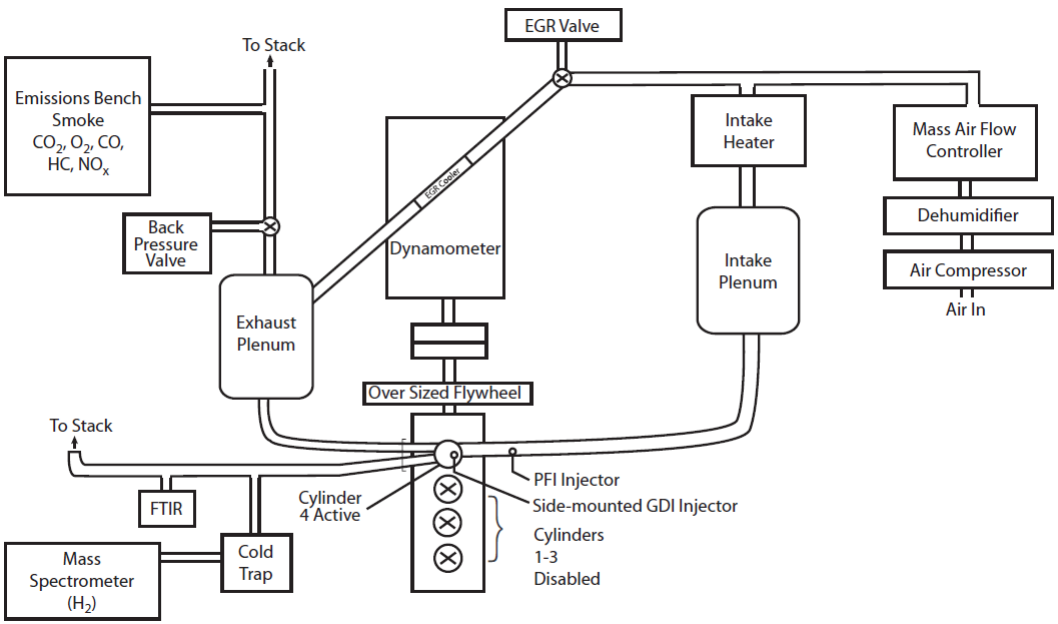
*California Energy Commission Report Publically Available At:
http://www.energy.ca.gov/2009publications/CEC-500-2009-011/CEC-500-2009-011.PDF

Bench Flow Reactor

TCR Reformer Catalyst

Parametric Experimental Investigation of In-cylinder TCR Completed with 5 Fuels

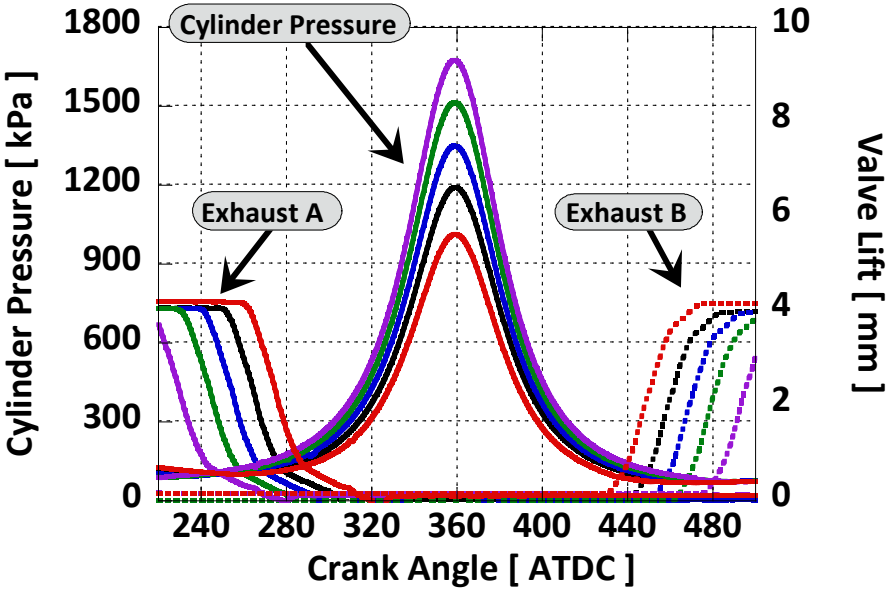
- Fuels: Iso-octane, methanol, ethanol, iso-butanol, and hydrous ethanol
- 5 different NVO durations at 2000 rpm: 120, 140, 160, 180, and 210 CA
- 3 different start-of-NVO conditions
  - High temperature, no O_2 available: setup by stoichiometric SI combustion without EGR
  - Reduced temperature, no O_2 available: setup by stoichiometric SI combustion with 20% EGR
  - Reduced temperature with 5% O_2 available: setup by lean SI combustion at λ=1.2
- Chemical speciation with FTIR and mass spectrometer

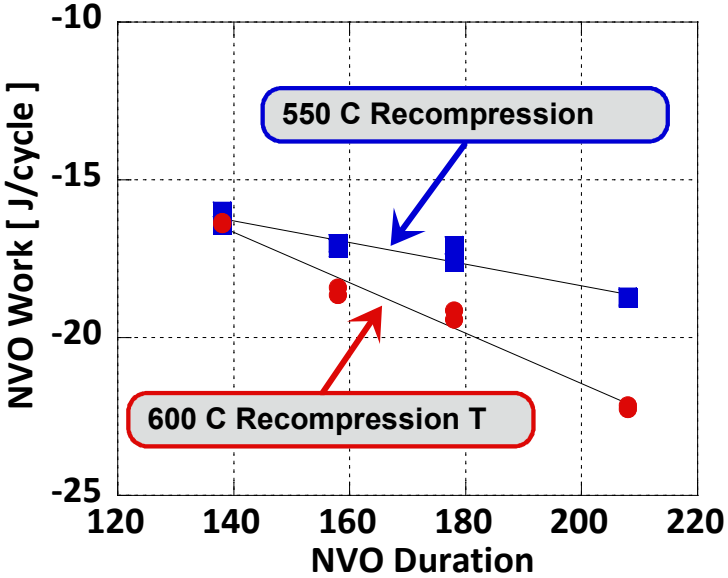


Work Input Required is Dependent on NVO Duration, Start of Recompression Conditions, and Fuel Type

Heat Losses Result in Work Input during Motored NVO

- Work increases with longer NVO and higher temperature at the start of recompression





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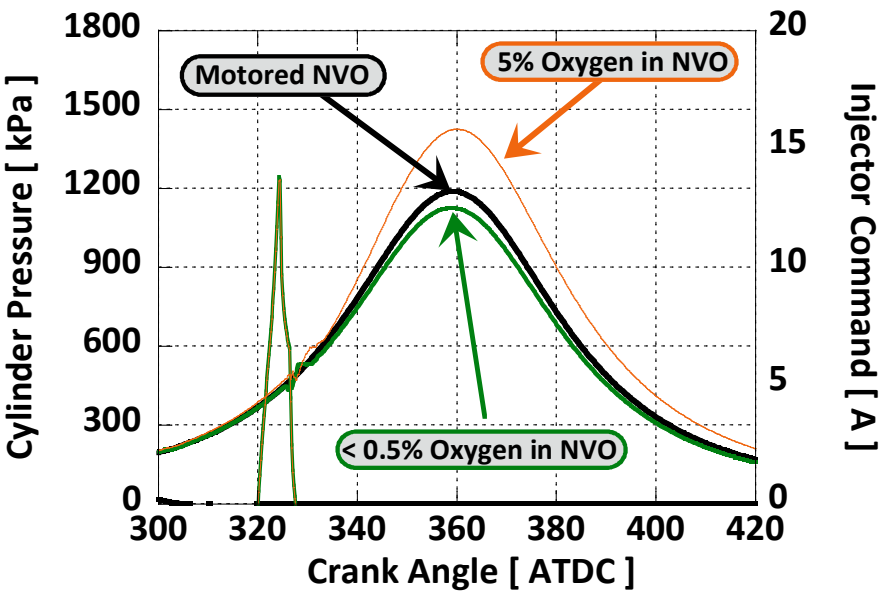
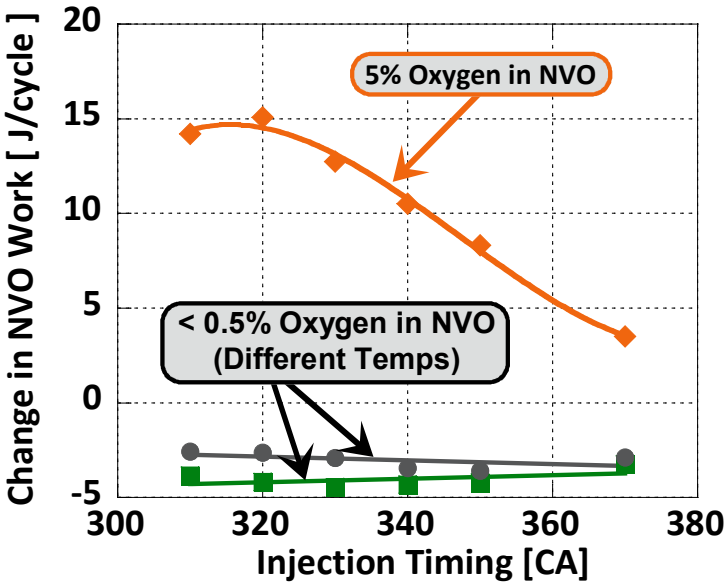
Work Input with Fuel Present is Dependent on Injection Timing, Oxygen Concentration

- Presence of oxygen allows combustion reactions to dominate, provides positive work out





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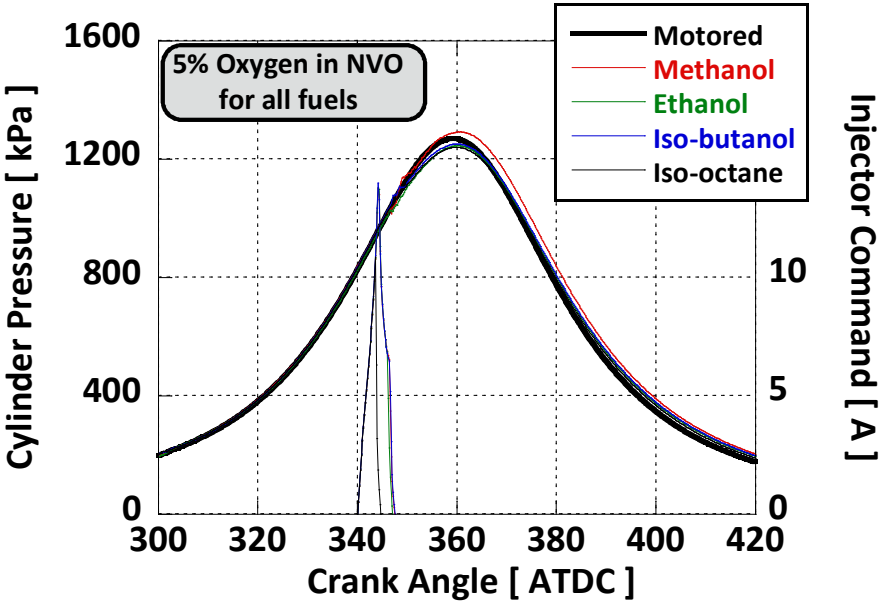
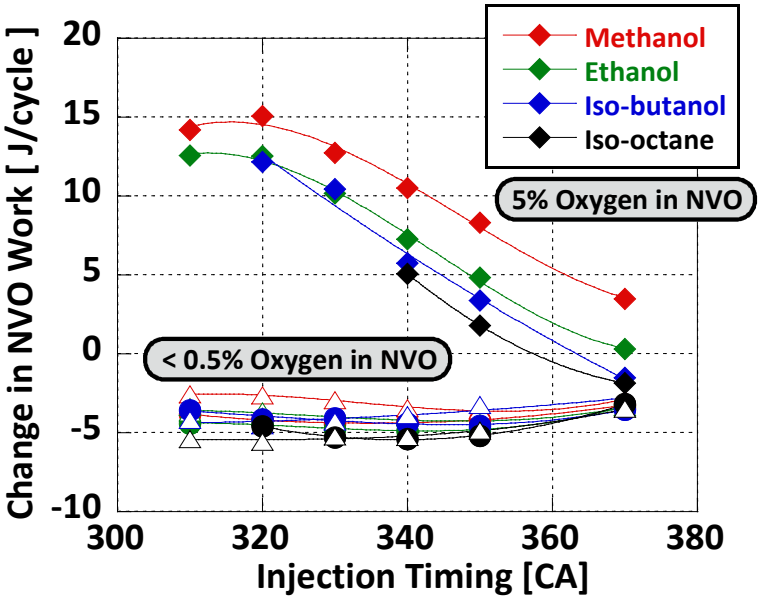
Work Input is Also Dependent on Fuel Type

- Iso-octane requires largest work input despite lowest latent heat of vaporization

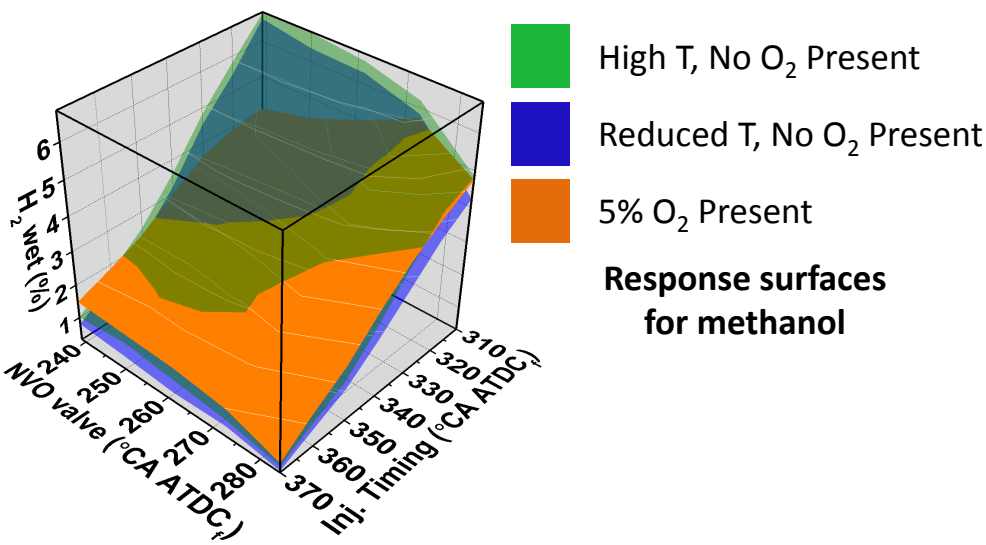




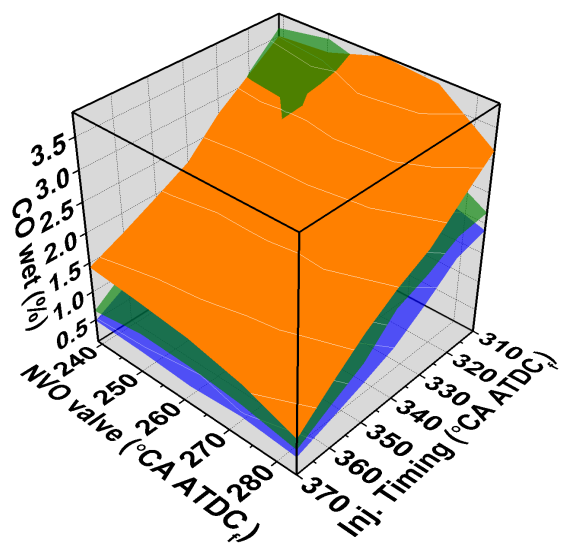
Significant Amounts of H_2 and CO Generated, Primary Dependencies are Fuel Type and Injection Timing

- CO and H_2 both increase with earlier fuel injection timing
  - Implies that reaction timescales are relatively slow
- Additional factors affecting the temperature/pressure history and chemistry are minor by comparison
  - NVO duration, start of recompression temperature, presence of oxygen
- Significant fuel-specific dependencies on H_2 and CO production
  - Methanol produces the most H_2 and CO, iso-octane produces the least

Hydrogen



Carbon Monoxide



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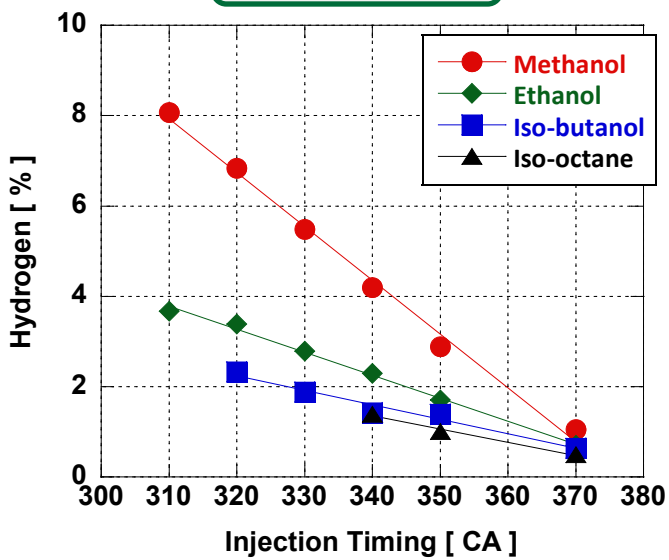

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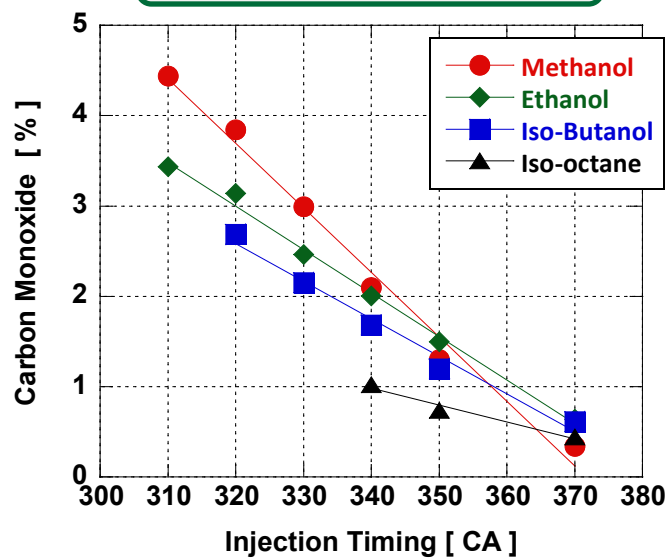
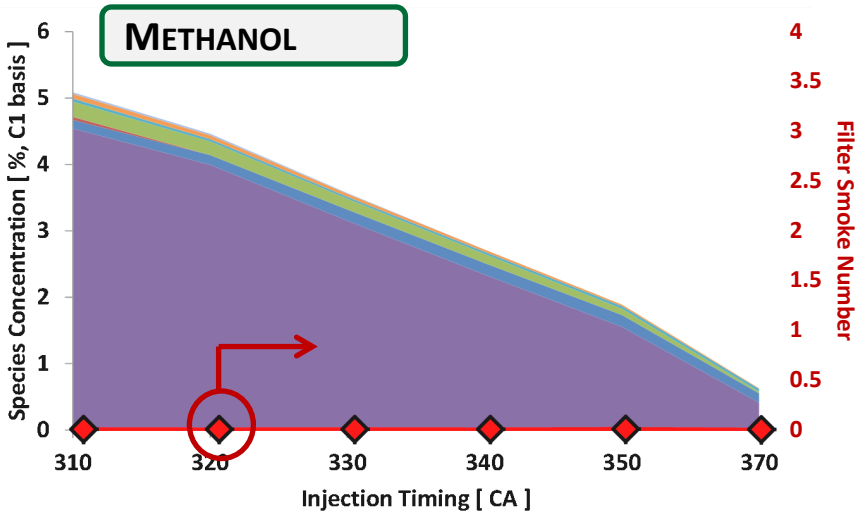
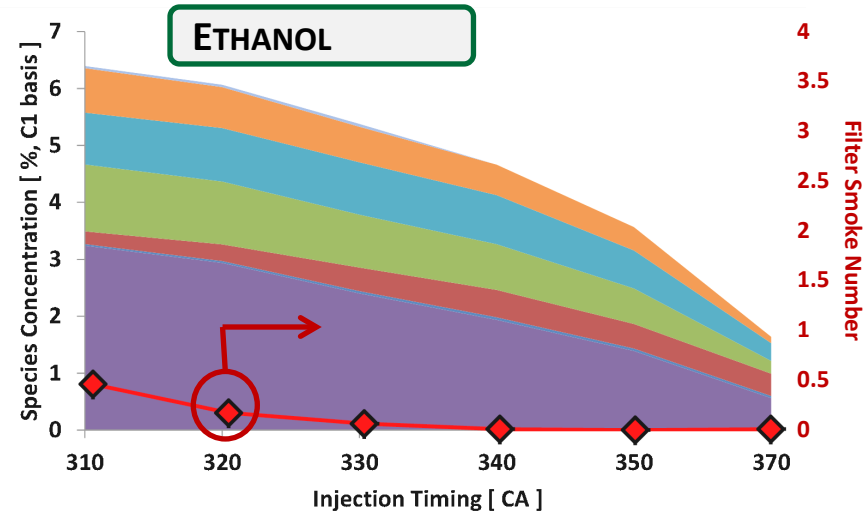
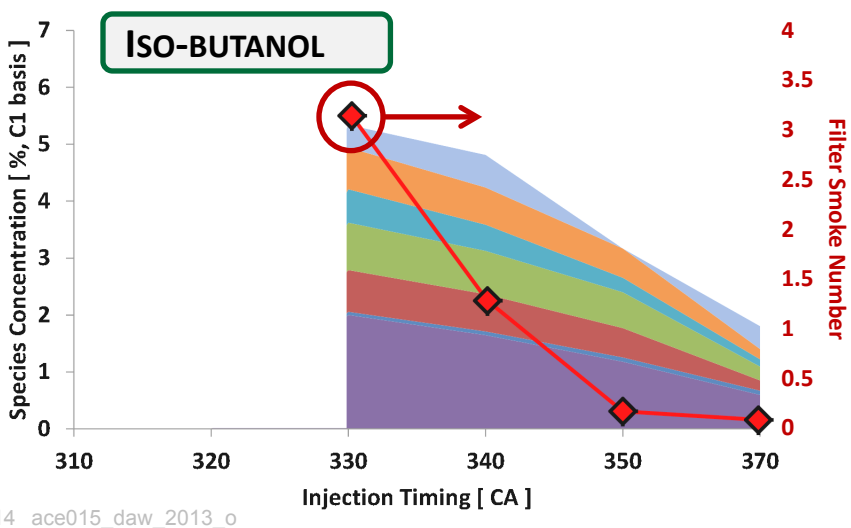


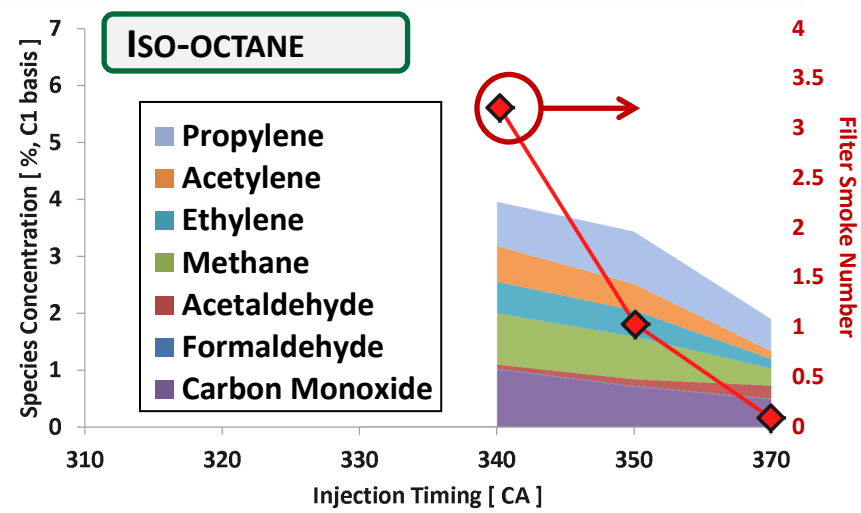
Conversion of Fuel Carbon to CO and Short Chain HC is Dependent on Injection Timing and Fuel Type

- Primarily CO produced for methanol, but short chain HC species dominate for ethanol, iso-butanol, and iso-octane
- Higher conversion for advanced injection, but soot limited in for some fuels



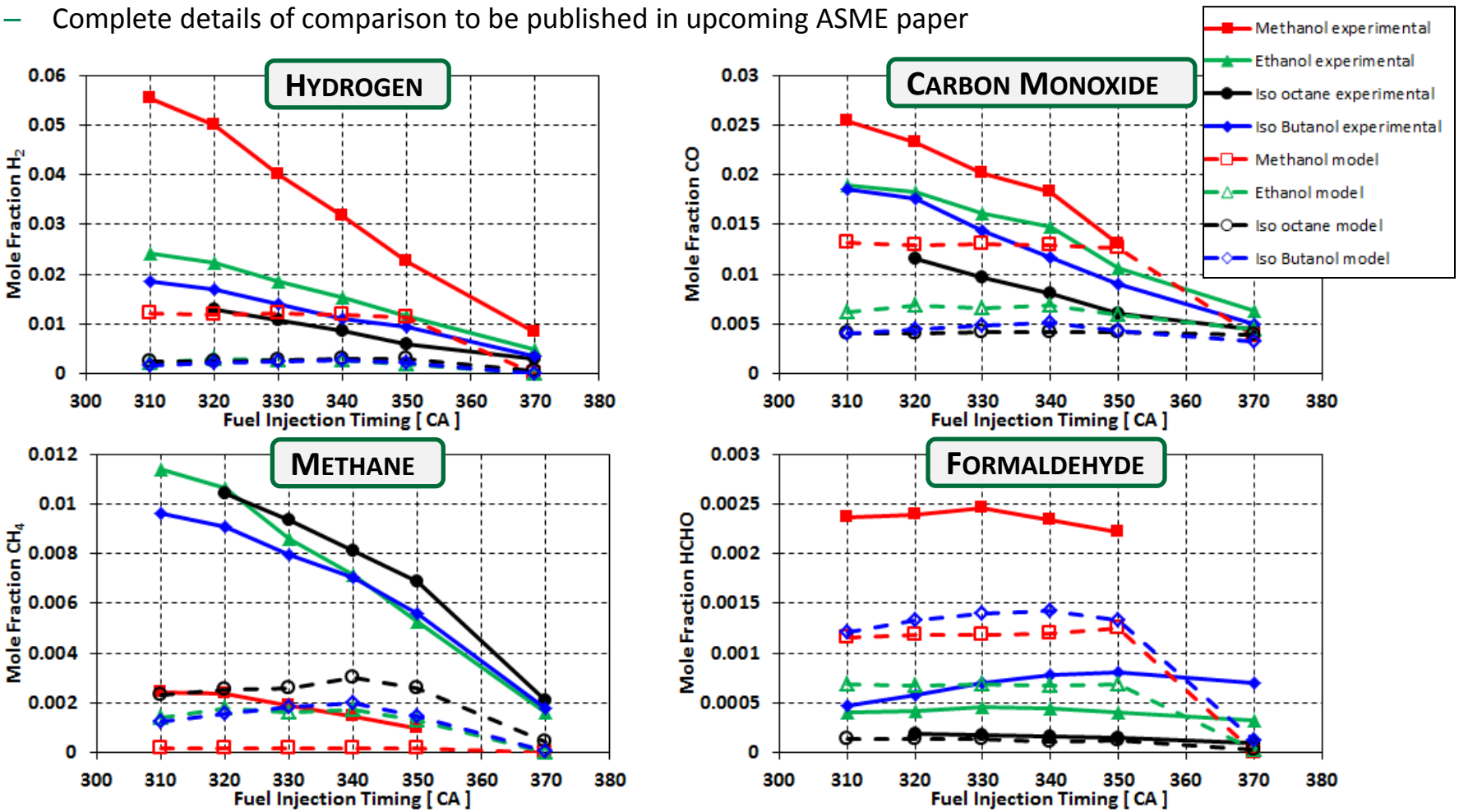






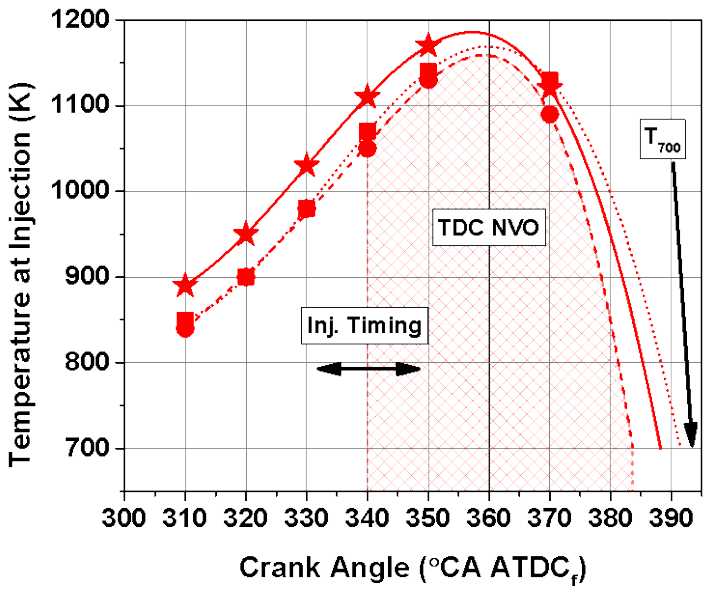
Available Kinetic Mechanism Do Not Agree Well with Experimental H_2, CO, and Hydrocarbon Measurements

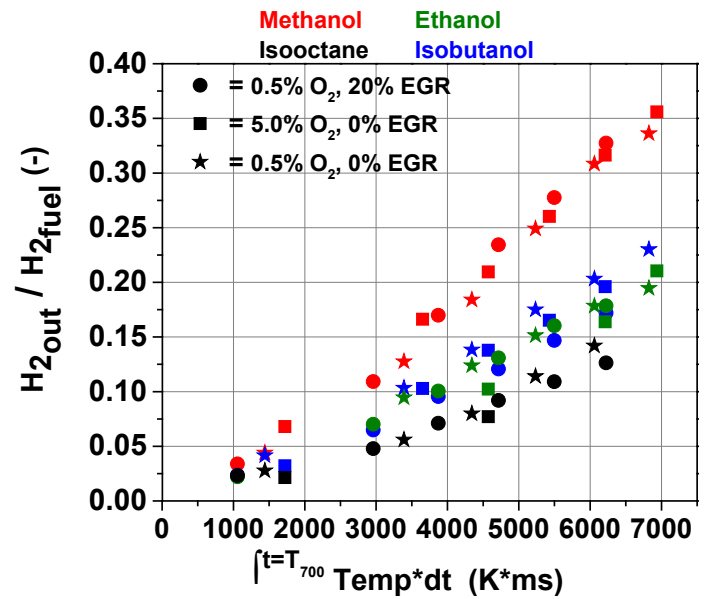
- Chemkin Pro® used with a variety of publically available kinetic mechanisms
  - Mechanisms generally under-predict, especially for H_2 production, because they are being extrapolated to fuel-rich zones where there is limited kinetic data
  - Complete details of comparison to be published in upcoming ASME paper



Hydrogen Production is Better Predicted by a Time Temperature Integral than Kinetic Models

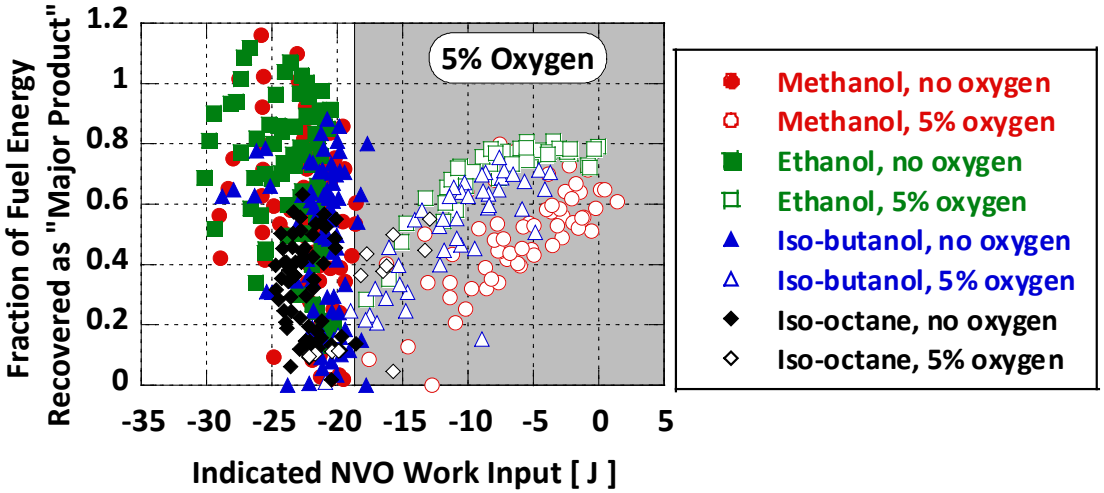
- Integrate time-temperature from injection to frozen chemistry (T=700 K)
  - Motored temperature history assumed, enthalpy of vaporization neglected
  - Methodology has parallels to Lawson Criterion for fusion reaction ignition as well as prediction of knock in spark ignition engines
- Hydrogen production is nearly linear with time-temperature integral
  - More than 1/3 of the fuel hydrogen converted to H_2 for methanol
  - Integral is equally valid for cases where oxygen is and is not present at start of NVO
- Hydrogen production shows significant fuel dependency
  - Methanol > Ethanol ≈ Iso-butanol > Iso-octane



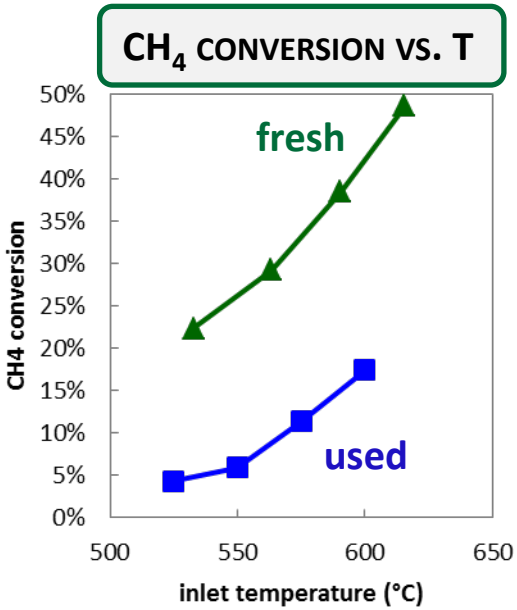


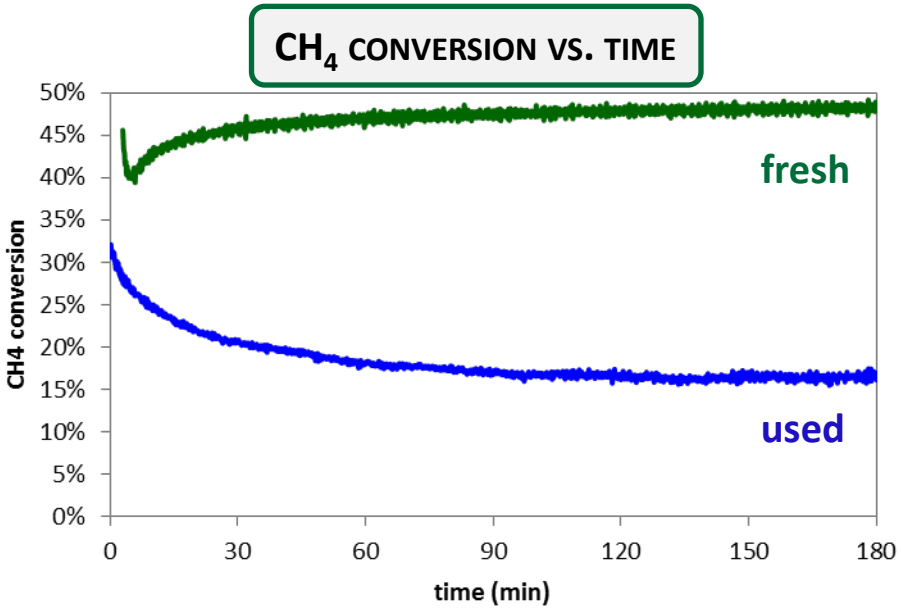
Are We Successfully Achieving TCR?

- Characterized fuel energy converted to "major species" relative to fuel energy injected, as quantified by mass spectrometer and FTIR
  - Major species defined as H_2, CO, methane, formaldehyde, acetaldehyde, ethylene, acetylene, propylene
  - Concentrations of unconverted fuel higher MW hydrocarbons are not resolved
- Fuel energy converted to major species can approach the LHV of the fuel energy input
  - Fuel energy of major species exceeds fuel energy input in some cases, needs to be confirmed
  - When oxygen was present, fuel energy converted to "major species" was limited to approximately 80%
  - Iso-butanol and iso-octane were limited in operating condition by smoke, unable to achieve same conversion
  - Conversion of fuel to major species appears to include chemical processes other than steam reforming
- Conversion of fuel to mixture high in H_2, CO, and methane through fuel-rich chemistry is not thermodynamically expensive



Pathway 2: Flow Reactor Experiments Reveal Differences Between Fresh and Used Catalyst Reforming Activity





fresh: as received by GTI from catalyst supplier

used: run on TCR system at Cummins

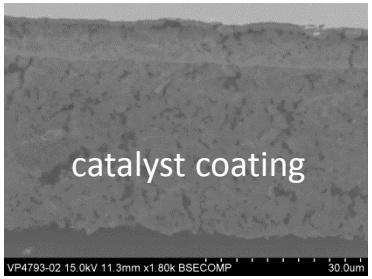
reforming conditions: 15.7% CH_4, 16% H_2O, 8% CO_2, balance N_2; SV: 3500 h^{-1}

- Used catalyst steady state CH_4 conversion much lower than fresh catalyst across reforming temperature window
- Fresh sample shows increasing reforming activity as catalyst auto-reduces
- Used catalyst performance degrades with operating time through unknown mechanism

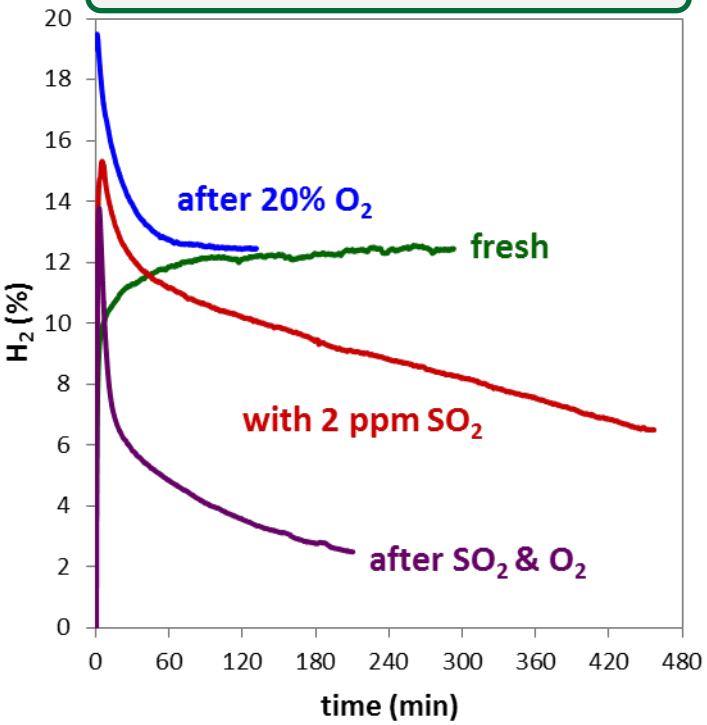
Sulfur Poisoning Appears to Be Most Likely Cause of Deactivation in Used Sample

- Potential catalyst deactivation mechanisms:
  1. Catalyst washcoat delamination/spallation
     - SEM images reveal intact catalyst
  2. Oxidation of Ni in catalyst by air during system shut down
     - Oxidation temporarily (and reversibly) increases reforming activity
  3. Sulfur poisoning
     - Low level (2 ppm) SO_2 exposure rapidly and irreversibly deactivates the catalyst
     - Further deactivation occurs after O_2 exposure of the S-poisoned catalyst
- Future experiments focused on understanding why small amount of SO_2 has large impact
- Goal: develop mitigation strategies or formulation changes that improve durability

SEM Image



H_2 at reformer outlet at 600 C



COLLABORATIONS

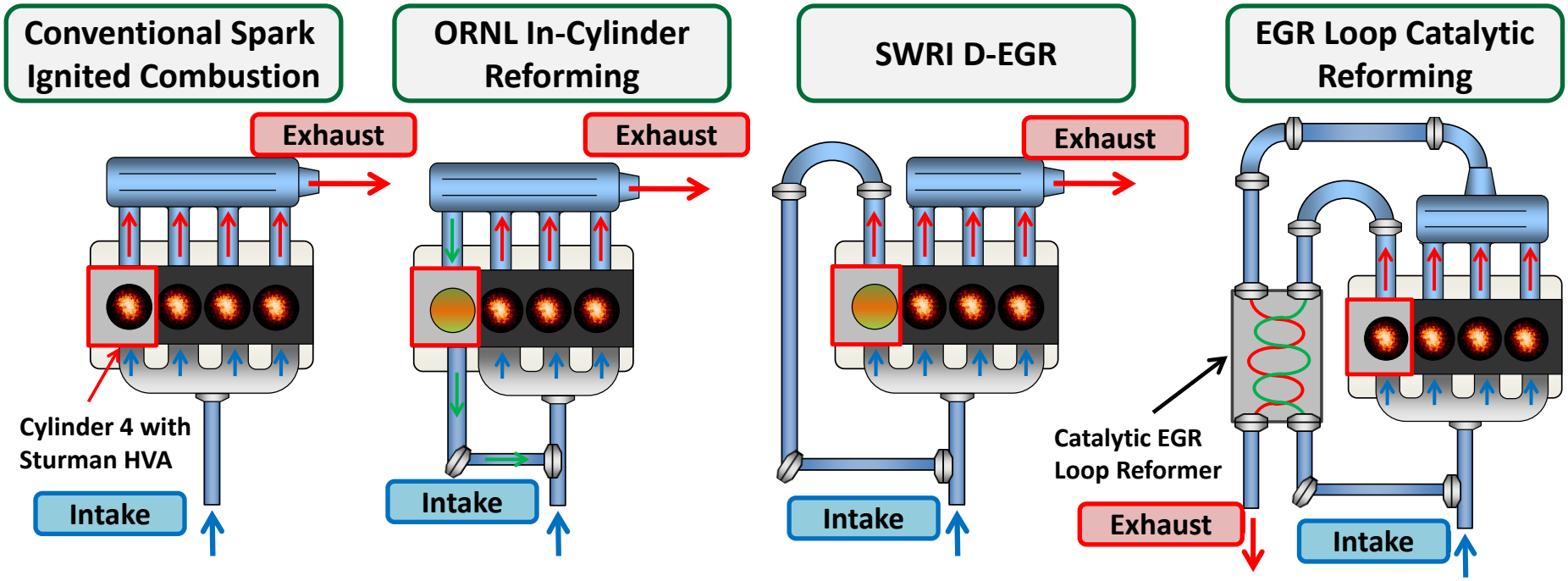
- 2010 USCAR Colloquium (overall direction)
  - 29 invited experts from industry, universities, labs and government to identify long-term research priorities regarding the theoretical and practical efficiency limits of internal combustion engines
  - Full report available at http://feerc.ornl.gov/pdfs/Stretch_Report_ORNL-TM2010-265_final.pdf
- Collaboration with Dick Steeper at SNL started 2012
  - Similar research interest and goals with regards to NVO chemistry
  - Sharing information on experimental and analytical techniques
  - Plans for data sharing and joint publications
- Collaboration with Gas Technology Institute (GTI) and Cummins
  - EGR loop TCR concept
  - Sharing experimental data and catalyst samples
- Sturman Industries
  - Modifications to system controls to allow 6-stroke engine cycle
- University Collaborations
  - Analysis of engine thermodynamics (Jerry Caton at Texas A&M University, and Dave Foster at the University of Wisconsin)
- Potential related funds-in project with OEM involving reforming

Fuel-rich In-cylinder Reforming and EGR Loop Reforming Remain Promising Pathways to High Efficiency

- In-cylinder reforming can produce high concentrations of high octane number components (H_2, CO, and methane)
  - Question of whether TCR was achieved has not yet been definitely answered
  - Experimental data shows that in-cylinder reforming is not thermodynamically expensive
  - Only a limited amount can be done with modeling because kinetic models do a poor job of predicting the fuel-rich chemistry of interest (we will be reaching out to kinetic modelers to share our data and concerns)
- Flow reactor experiments will focus on improving durability of reforming catalysts prior to use in engine experiments
  - Determine why small sulfur loadings result in dramatic deactivation
  - Develop mitigation strategies or formulation changes that will improve sulfur tolerance
- Future work will be expanded to include the advantageous properties of reformate
  - Hydrogen enables stable combustion in dilute environments due to high flame speed
  - Improved anti-knock properties of reformate and EGR allow higher compression ratio
  - High dilution and lower combustion temperature are thermodynamically favorable
    - Increases in the ratio of specific heat (γ) due to both lower temperature and composition of gas (dilution through EGR and/or lean operation)
    - Reduced heat losses with lower temperature environment

Continuing Work will Apply Current Methodologies to Multi-Cylinder Engine Experiments

- Application of in-cylinder fuel-rich chemistry relies on multi-cylinder engine strategy where cylinders operate differently
  - Move Sturman HVA system from single-cylinder engine to cylinder 4 on a multi-cylinder engine to maintain experimental flexibility
  - Maintain 2.0L GM Ecotec® engine platform, use existing engine installation at ORNL



- 2-year process to evaluate these combustion concepts on multi-cylinder platform
- Continue to apply unique ORNL analytical capabilities and thermodynamic analyses

Summary

Relevance

Investigate high risk revolutionary combustion strategies with potential for large efficiency increases

Approach: Two Pathways to Achieve Fuel Reforming

- In-cylinder non-catalytic reforming (6-stroke engine experiments)
- EGR loop catalytic reforming (catalyst evaluation and characterization)

Accomplishments

- Speciated exhaust composition and characterized the effects of initial conditions and fuel composition on in-cylinder reforming over a variety of conditions
- Revealed limitations of current kinetic models under fuel-rich conditions
- Identified sulfur poisoning as likely deactivation mechanism for GTI EGR loop TCR catalyst

Collaborations

- Active collaboration with Industry, a National Laboratory, and Universities

Future Work

- 2-year effort to investigate the various combustion concepts involving reforming on a common multi-cylinder engine platform
- Apply unique ORNL analytical capabilities and thermodynamic analysis