Development of Gas Fuel Interchangeability Criteria for Combustion Systems

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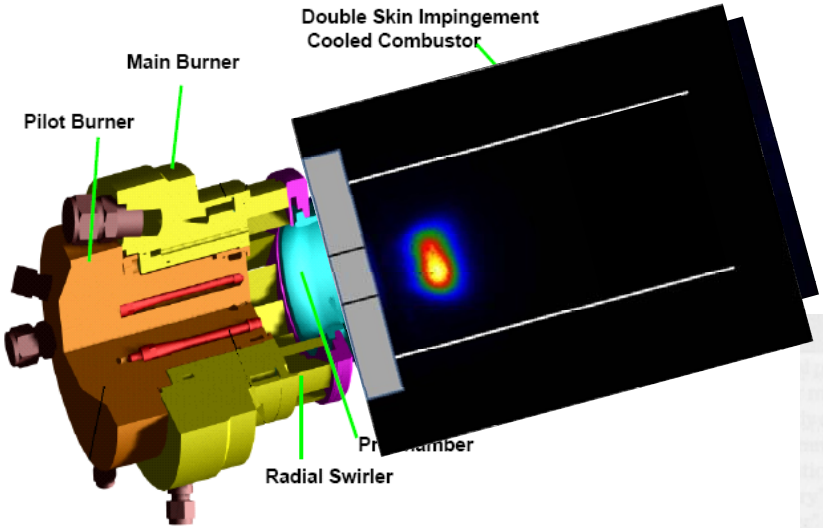
(CEC Contract 500-08-034; Marla Mueller)

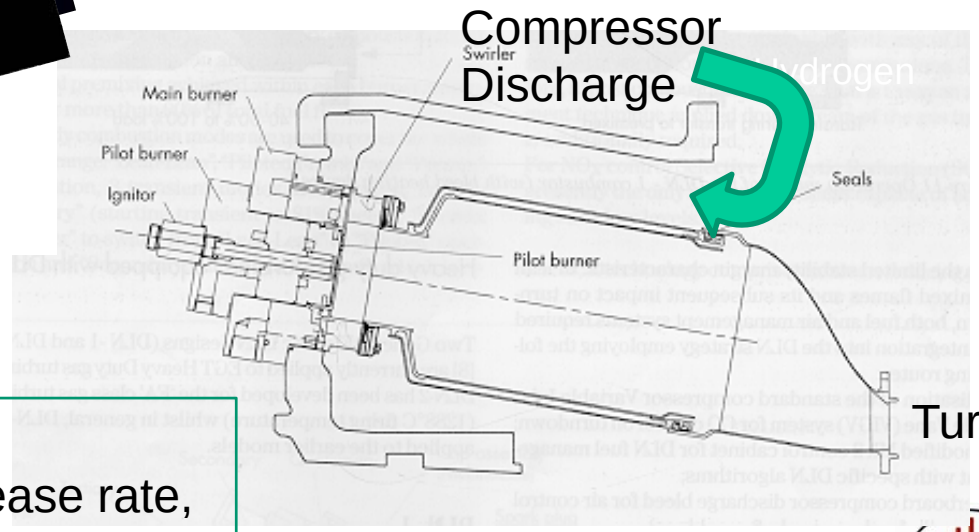
Motivation

- **What accommodations are needed for advanced combustion systems to use various fuels?**
  - **Example: Hydrogen containing fuels in a NG system**



OH* visualization (Heat release marker)
Reaction Structure
T_{ad} = 1780 deg-K

Substantially <u>different reaction structure</u> for different fuels with same firing temperature

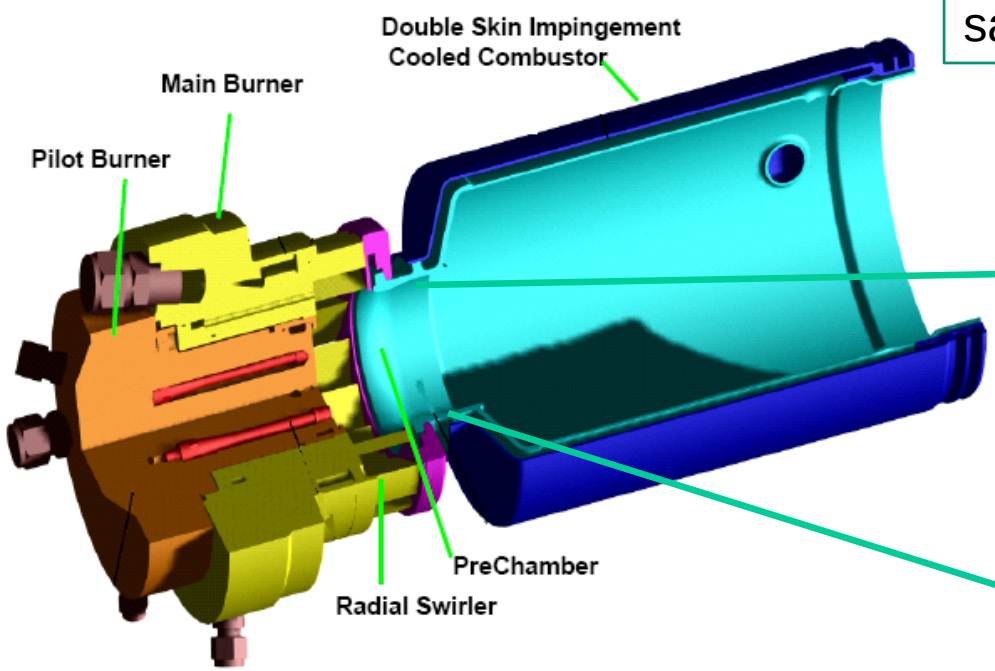


Implications for emissions?
Ignition time, flame speed, heat release rate, heat release chemistry

Motivation

- **Implications for Operability?**
  - **Blowoff, Flashback**

Substantially different flame speed for different fuels with same firing temperature

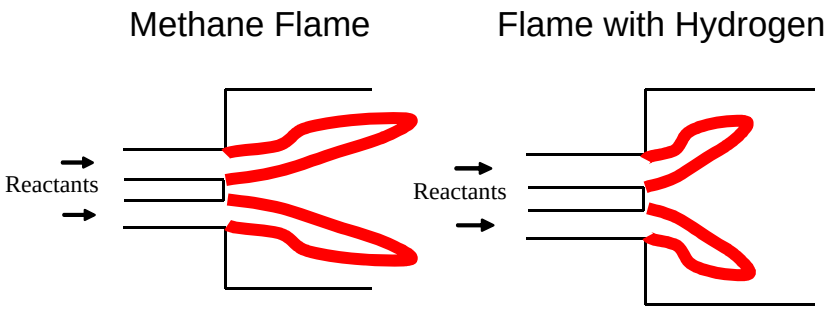


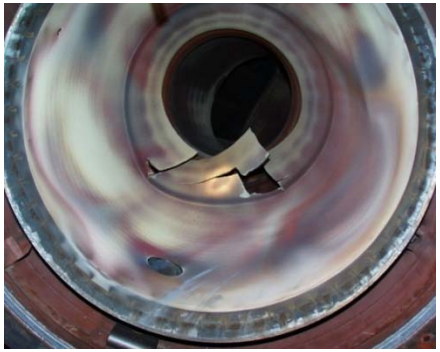
Flashback or autoignition w/high hydrogen content fuel damaged prechamber

Prediction of ignition behavior and flame speed critical

Motivation

- **Implications for Operability?**
  - **Acoustic Oscillations**





Substantially <u>different flame speed, ignition time and reaction rates</u> for different fuels with same firing temperature leads to <u>different flame position</u>

Flame position can couple heat release dynamics w/ pressure dynamics→can lead to combustion oscillations

Ignition, heat release rates, flame speed

Gas Fuel Interchange

- **Overall Goal: Develop/validate gas fuel interchangeability criteria (GFIC) for various fuel classes (for lean premixed systems—i.e. advanced combustion systems)**
  - **Increasing interest in <u>fuel flexibility</u> and <u>transient response</u>**
  - **Focused on end use perspective vs supply side (e.g. Wobbe)**
- **Objectives/Outcomes**
  - **Quantify/measure flame speed, ignition, flashback, blowout, emissions characteristics for fuels of interest**
    - **Literature/ongoing projects (e.g. USC, Princeton, Texas A&M)**
    - **"Fundamental" Test Rigs (UCI, GaTech, Univ of Wash)**
    - **"Benchmark" Data**
  - **Compile data/measure/analyze data → use to address questions**
    - **Design Guides**
    - **Impact on Equipment operability**
    - **Impact on air quality, GHG emissions**
    - **Coupled operability and emissions questions**

Gas Fuel Interchange

- **Example guides: correlations / relations / methodologies for**
  - **Ignition Delay time [fuel type, composition, conditions]**
    - **Keys--reaction rates, induction time, ……**
  - **Flashback Propensity [fuel type, composition, conditions]**
    - **Keys--Flame speeds, diffusivity, quenching, strain….**
  - **Stability Limits [fuel type, composition, conditions]**
    - **Keys--Time scales, turbulent flame speed, reaction rates, strain….**
  - **Criteria pollutant emissions [fuel type, composition, conditions]**
    - **Keys--Kinetics, mechanisms, reaction rates, time scales….**
- **Stand alone guides (e.g., Excel) or "hybridized" with CFD / simulation platforms**
  - **Models to assess/infer how equipment responds to fuel characteristics**
    - **operability**
    - **emissions**

Project Tasks

- **Task 1—Administration**
  - **Project Advisors**
- **Task 2—Coordination & GFIC Development**
- **Task 3—Chemical Mechanism Work (UW)**
- **Task 4—Ignition/Flashback/Blowoff Work (UCI)**
- **Task 5—Turbulent Flame Speed Work (GT)**

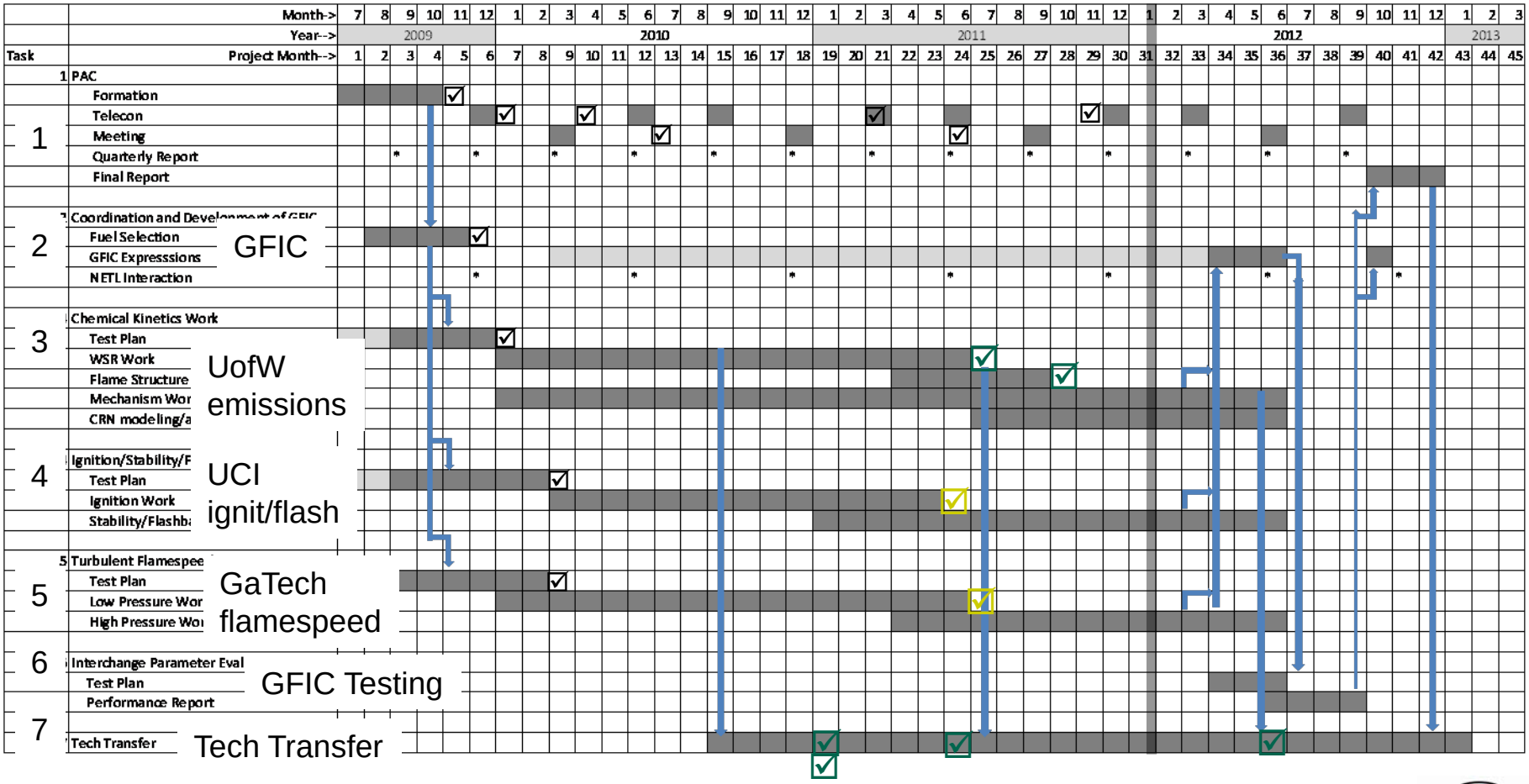
3 years
>80% of
effort

- **Task 6—Interchange Parameter Testing**

- **Task 7—Technology Transfer**

Project Tasks

- **Current Status**

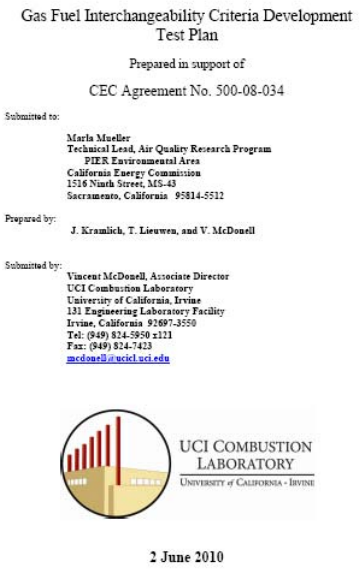


Fuel Selection

- **20 November 2009 Fuel Selection Report prepared and distributed**
- **9 Dec 2009 webinar**

- **Based on 9 Dec 09, 24 Mar 10 webinars, 4 May 2010 revision**
  - **Included Details on Test Plans**
  - **Distributed to Advisors**

- **2 June 2010 version prepared based on final input from Advisors**



Gas Fuel Interchangeability Criteria Development Test Plan

Prepared in support of

CEC Agreement No. 500-08-034

Submitted to:

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UNIVERSITY of CALIFORNIA - IRVINE

2 June 2010

Gas Fuel Interchange Matrix

- **Consensus Fuels / Compositional Ranges**

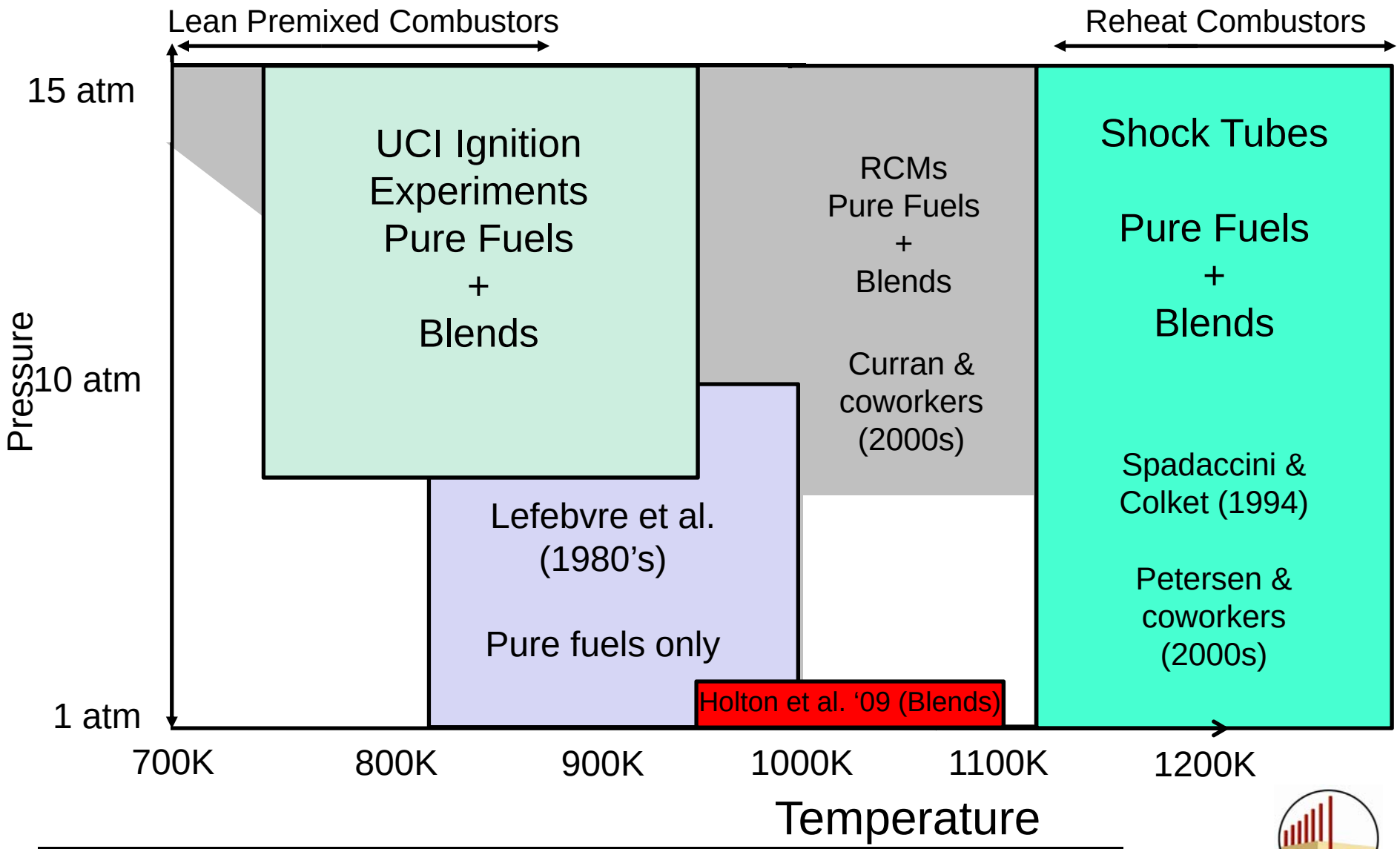
Source	H2	CO	CH4	CO2	N2	C2	C3
High H2	90- 100	0 - 10					
Process and Refinery Gas	25 - 55	0 - 10	30 - 65	0 - 5		0 - 25	0 - 25
Gasified Coal/Petcoke (O2 Blown)	35 - 40	45 - 50	0 - 1	10 - 15	0 - 2		
Gasified Biomass (air blown) & Gasification w/ N2 Dilution	15 - 25	15 - 35	0 - 5	5 - 15	30 - 50		
Landfill / Digester			35 - 65	35 - 55	0 - 20		
LNG			86- 97		0 - 3	2 - 11	0 - 2
Shale Gas			82-97	0-3		0 - 14	0 - 1
Associated Gases			75- 95			5 - 25	

Example Results

- **Focus on Alkanes (i.e., LNG)**
  - **Autoignition Interchange Criteria**
    - **Design Guides to predict time to ignition**
      - Implications for burner/turbine premixer design
      - Implication for knock in automotive applications
  - **Fuel Interchange impacts on emissions**
    - **“Entitlement” (important relative to regulatory guidance)**
    - **Impact evaluation methodology**

- **Influence of Hydrogen Content**
  - **Emissions “entitlement”**

Ignition Delay Data Space



Details of Data/Analysis

- **Beerer, et al. (2011): An Experimental Ignition Delay Study of Alkane Mixtures in Turbulent Flows at Elevated Pressures and Temperatures, *J. Engr Gas Turbines and Power*, Vol 133 pp 011502-1:8.**

- **Beerer and McDonell (2011): An Experimental and Kinetic Study of Alkane Autoignition at High Pressures and Intermediate Temperatures, *Proceedings of the Combustion Institute*, Vol 33 pp. 301-307. (and supplemental material)**

Two Types of Expressions

- **Correlation Based (suitable for EXCEL, Matlab)**
  - **Specific fuel mixes**
  - **Generalized approach**

- **Validation data for comprehensive chemical kinetic studies**
  - **Chemkin, Cantera, DARS, etc**
  - **Chemistry model for CFD**

Arrhenius Correlations for Each Fuel

Fuel	Composition	Ignition Delay Expression
1	Methane	$\tau = 9.08 \times 10^{-5} \cdot \exp\left(\frac{18.425}{RT}\right) P^{-1.0}$
2	Ethane	$\tau = 5.71 \times 10^{-9} \cdot \exp\left(\frac{33.540}{RT}\right) P^{-1.0}$
3	Propane	$\tau = 3.29 \times 10^{-8} \cdot \exp\left(\frac{29.765}{RT}\right) P^{-1.0}$
4	90% Methane, 10% Ethane	$\tau = 1.66 \times 10^{-6} \cdot \exp\left(\frac{24.865}{RT}\right) P^{-1.0}$
5	85% Methane, 15% Ethane	$\tau = 1.19 \times 10^{-6} \cdot \exp\left(\frac{25.410}{RT}\right) P^{-1.0}$
6	70% Methane, 30% Ethane	$\tau = 2.41 \times 10^{-8} \cdot \exp\left(\frac{31.590}{RT}\right) P^{-1.0}$
7	95 % Methane, 5% Propane	$\tau = 7.41 \times 10^{-6} \cdot \exp\left(\frac{21.750}{RT}\right) P^{-1.0}$
8	90 % Methane, 10% Propane	$\tau = 2.30 \times 10^{-7} \cdot \exp\left(\frac{27.435}{RT}\right) P^{-1.0}$
9	70 % Methane, 30% Propane	$\tau = 2.76 \times 10^{-6} \cdot \exp\left(\frac{22.330}{RT}\right) P^{-1.0}$
10	70% Methane, 15% Ethane, 15% Propane	$\tau = 8.05 \times 10^{-8} \cdot \exp\left(\frac{28.660}{RT}\right) P^{-1.0}$
11	Simulated Natural Gas	$\tau = 1.15 \times 10^{-8} \cdot \exp\left(\frac{33.120}{RT}\right) P^{-1.0}$
12	Irvine Natural Gas	$\tau = 7.44 \times 10^{-7} \cdot \exp\left(\frac{25.750}{RT_{mix}}\right) P^{-1.0}$

Generalized Correlation

- **Generalized**

A method to find an expression for the ignition delay of an 85/15 (by volume) mixture of methane and propane.

Fraction of propane in fuel: $f=0.15$

$$E_{85/15} = 18.4 + 3.8 \cdot (0.15)^{0.08} + 7.3 \cdot (0.15)^{2.5} = 21.7 \ \text{kcal/mol}$$

$$\log_{10}(A) = -4.04 - 1.55 \cdot (0.15)^{0.13} - 1.9 \cdot (0.15)^{2.4} = -5.27$$

$$A_{85/15} = 10^{-5.27} = 5.37 \times 10^{-6}$$

Hence,

$$\tau_{85/15} = A \exp\left(\frac{E}{RT}\right) P^{-1.0} = 5.37 \times 10^{-6} \cdot \exp\left(\frac{21.7}{RT}\right) P^{-1.0}$$

To find the ignition delay time of a 85/15 methane/propane mixture at 15 atm and 900 K, plug conditions into the expression

$$\tau_{85/15} = 5.37 \times 10^{-6} \ \text{atm s} \cdot \exp\left(\frac{21.7 \ \text{kcal/mol}}{1.987 \times 10^{-3} \ \text{kcal/mol K} \cdot 900 \ \text{K}}\right)(15 \ \text{atm})^{-1.0}$$

$$= 0.067 \ \text{s} = 67 \ \text{ms}$$

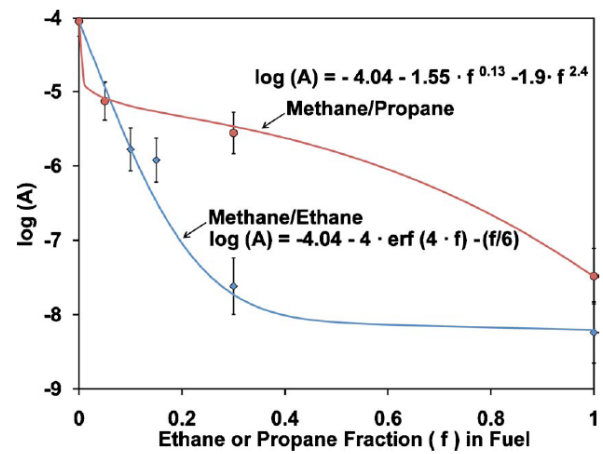
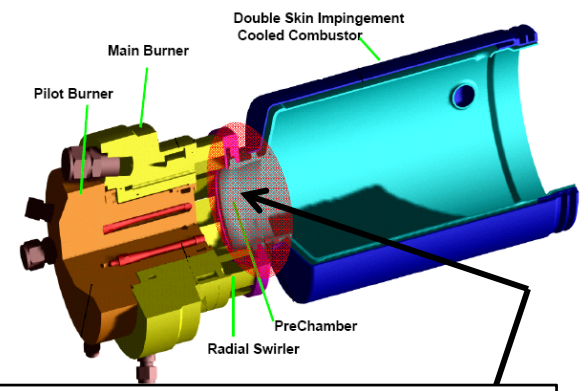


Fig. 12 Interpolation of the pre-exponential factor, *A*, of binary methane/ethane and methane/propane blends as a function of ethane or propane fraction in the fuel



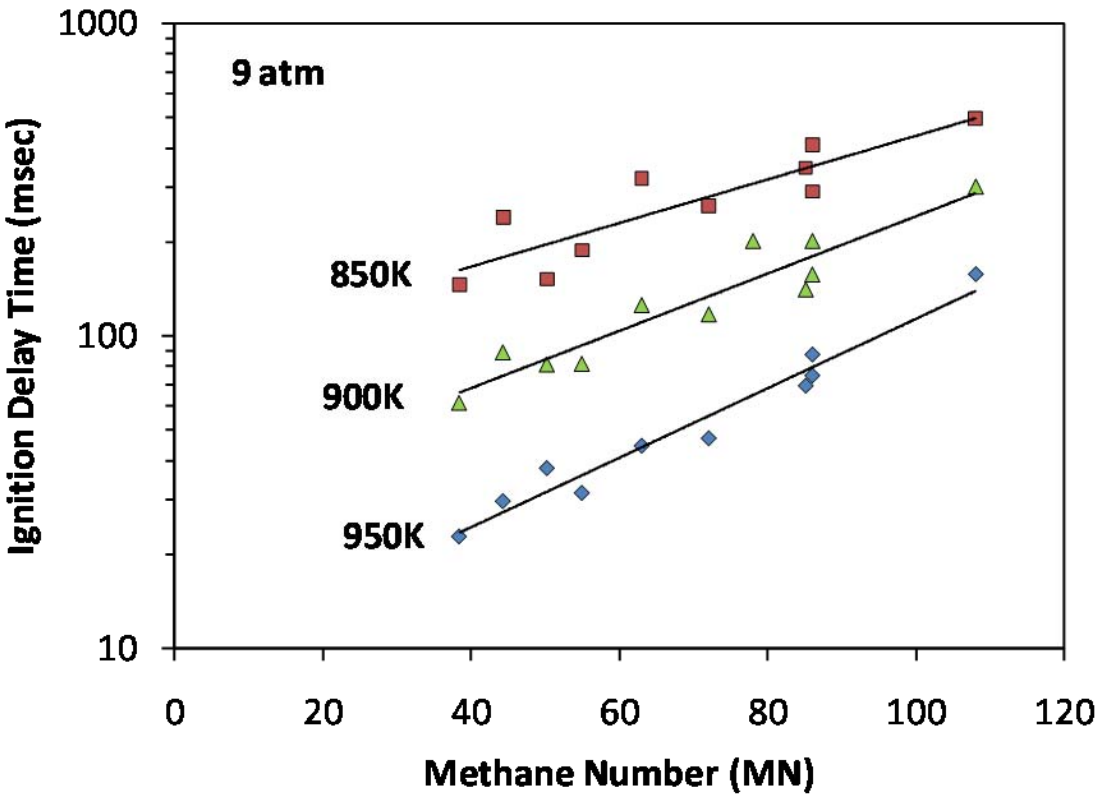
How much time can I allow for premixing If my fuel is XXX?

Beerer et al., 2011

Ignition Delay Time / Methane Number

Automotive Application

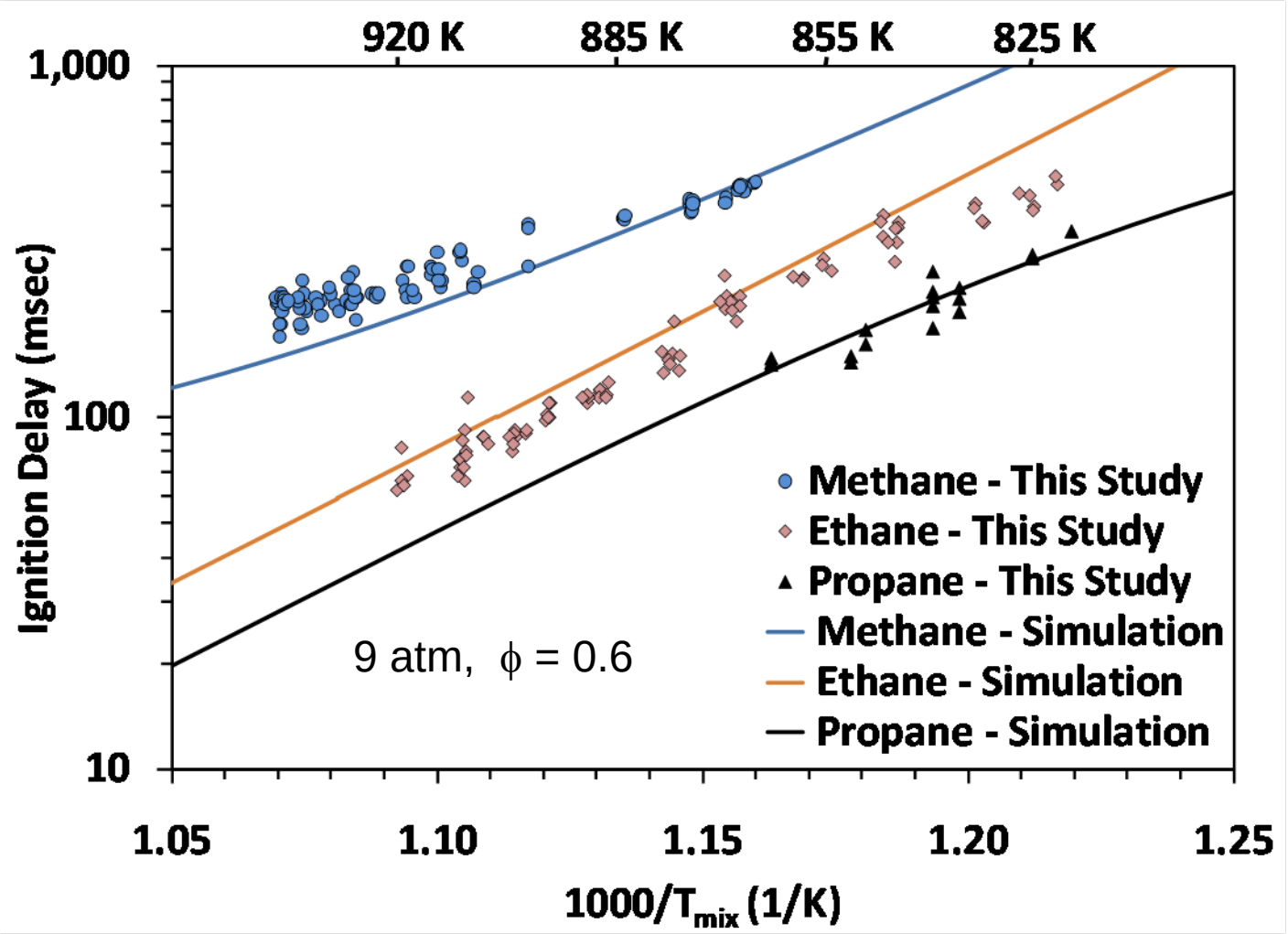
- MN is measure of knock resistance
  - ON: n-hept = 0
    iso-oct = 100
  - MN: H_2 = 0, CH_4 = 100
- Calculated MN for twelve fuels used in this study and calculated ignition delay times from correlations
- For fixed pressure and temperature, the ignition delay time scales with the Methane number



- Makes sense – longer the delay time → harder to ignite → high knock resistance
- Fuel Interchangeability: Same ignition delay for same M.N.? (e.g. CH_4 vs $CH_4/C_2H_6/CO_2$ mix)

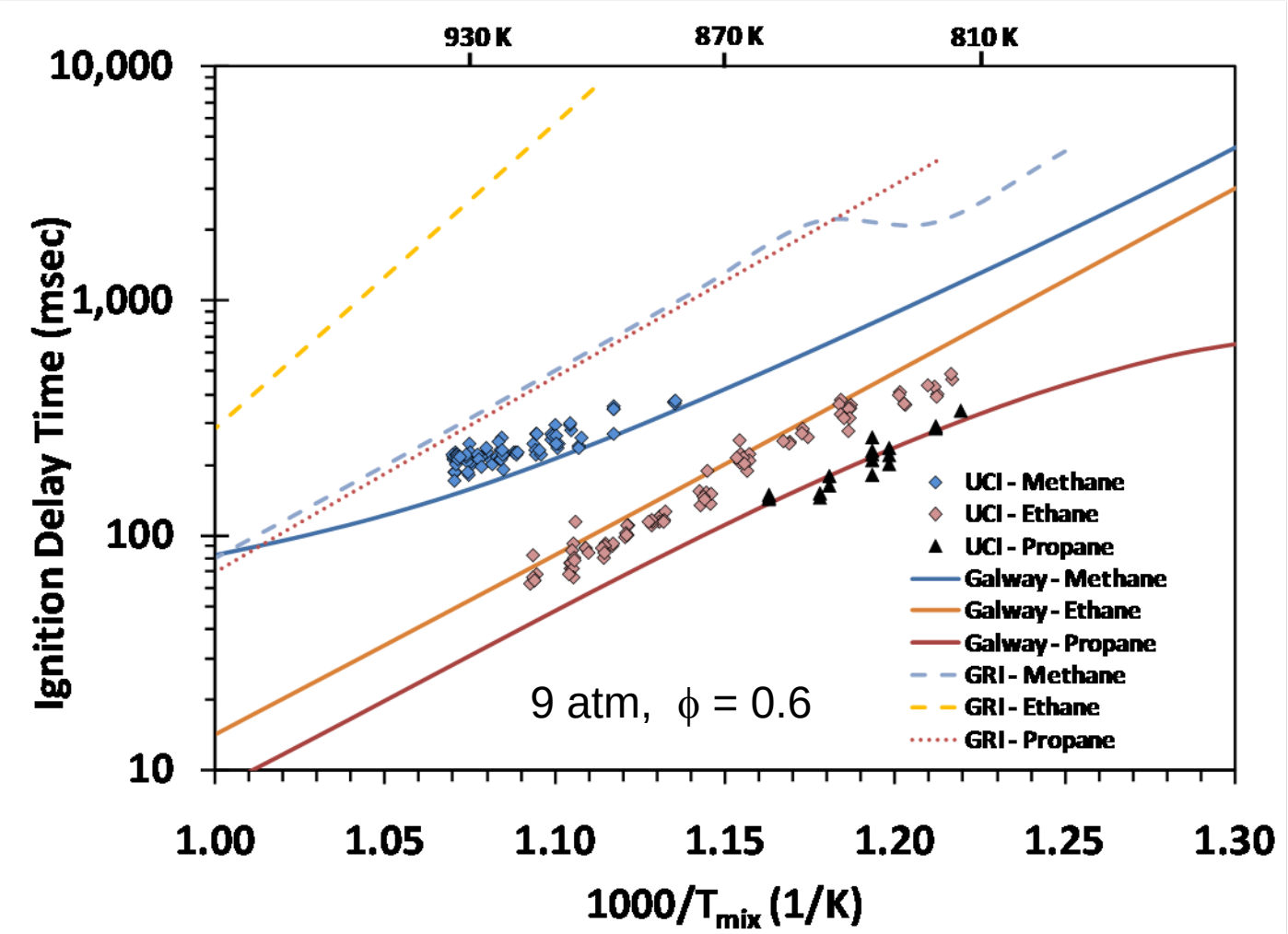
Validation of Detailed Kinetics

- Modeled in CHEMKIN and DARS with Galway C_3 Mechanism
- Kinetics simulation Assumptions:
  - Plug flow
  - Isobaric
  - Homogenous
  - Zero – Dim.
  - No wall effects
- CHEMKIN model can be used as a design tool to predict accurately ignition delays for alkane fuels at GT conditions.



Validation of Detailed Kinetics

- Galway Mech. Includes low temperature chemistry of alkanes up through C_3
- GRI Mech. designed for high temperatures and natural gas, not for pure ethane, propane.
- GRI not recommended at these conditions



Example Results

- **Focus on Alkanes (i.e., LNG)**
  - **Autoignition Interchange Criteria**
    - **Design Guides to predict time to ignition**
      - Implications for burner/turbine premixer design
      - Implication for knock in automotive applications
  - **Fuel Interchange impacts on emissions**
    - **"Entitlement" (important relative to regulatory guidance)**
    - **Impact evaluation methodology**

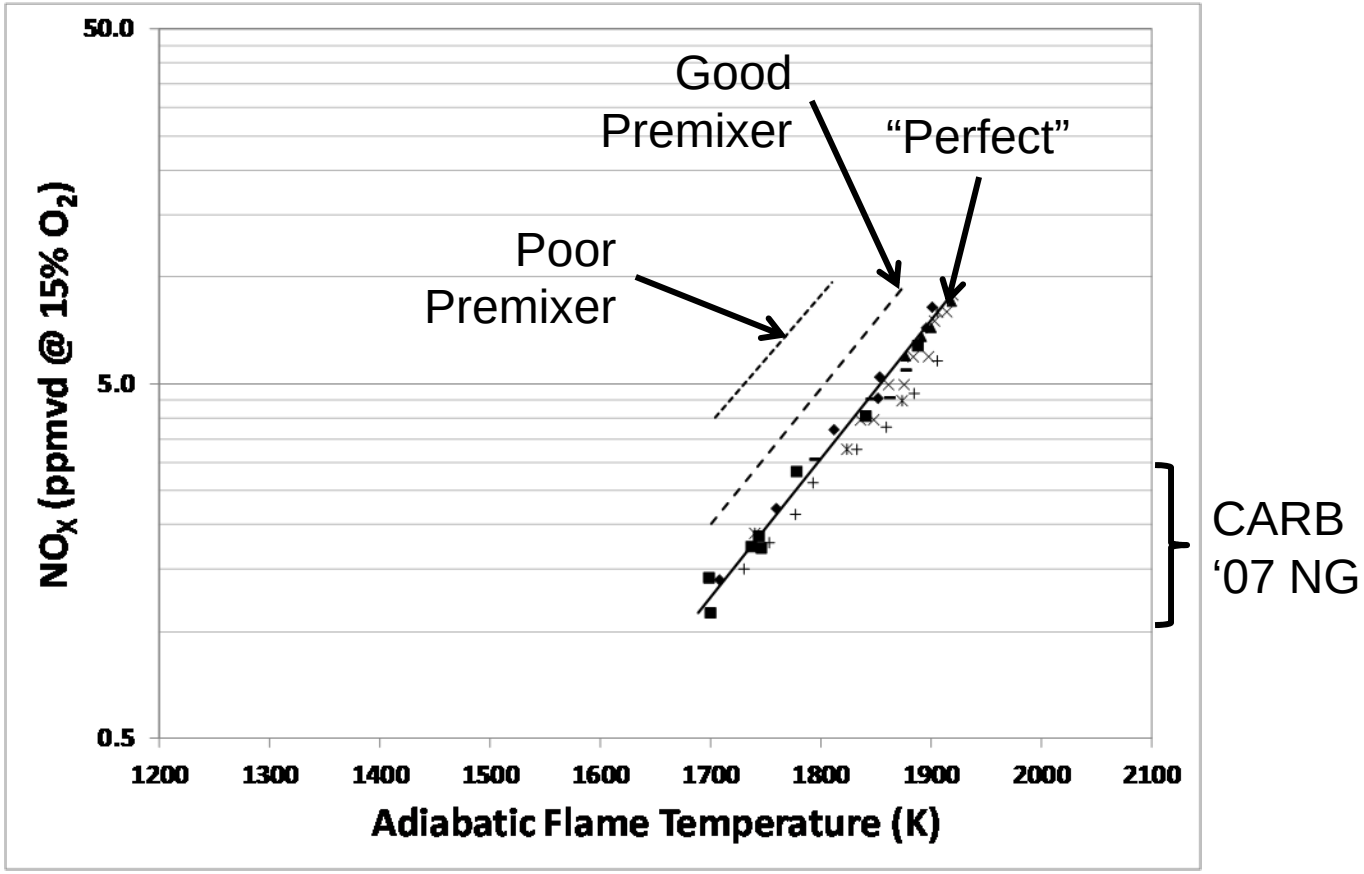
- **Influence of Hydrogen Content**
  - **Emissions "entitlement"**

“Entitlement” NOx Levels

- **Attributed to Leonard and Stegmaier (1994) from development study for GE advanced lean premixed natural gas fired gas turbines.**
  - **1-30 bar,**
  - **300-800 K inlet temps,**
  - **2-100 ms residence time,**
  - **various flameholders,**
  - **fully premixed fuel and air**
- **Goal: Establish a “target” for their designers**
- **Outcomes of L&S study of Lean Premixed Combustion**
  - **NOx *not* dependent on (1) pressure, (2) inlet temperature or (3) residence time**
  - **Paradigm shift at the time relative to NOx and combustion**
- **Corollary: Can be used to infer minimum expected NOx for lean premixed combustions systems—potential input to regulatory decisions**
  - **Many examples in the literature comparing to L&S for given design to comment on quality of design**

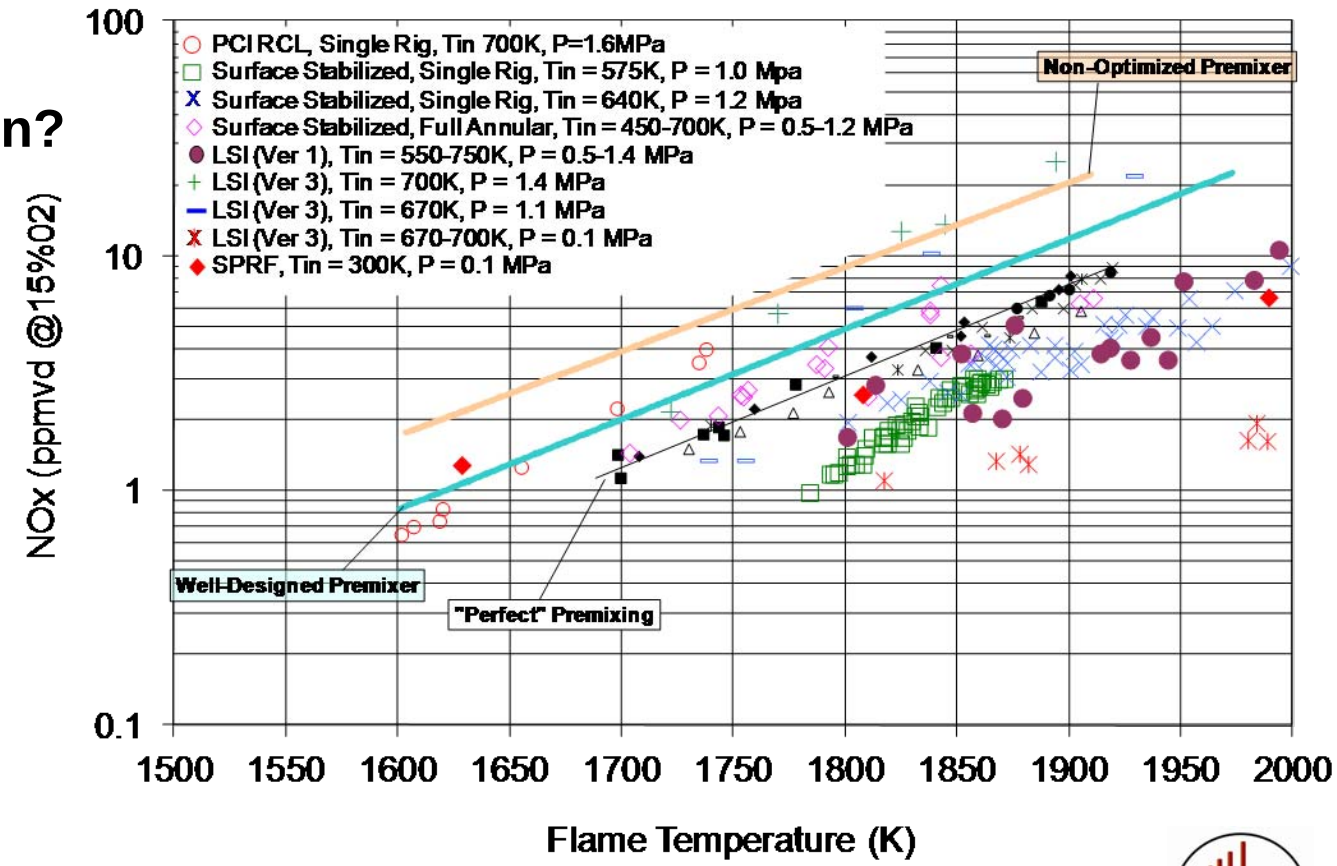
"Entitlement" NOx Levels

- **Entitlement Plot: Natural Gas (upstate NY)**



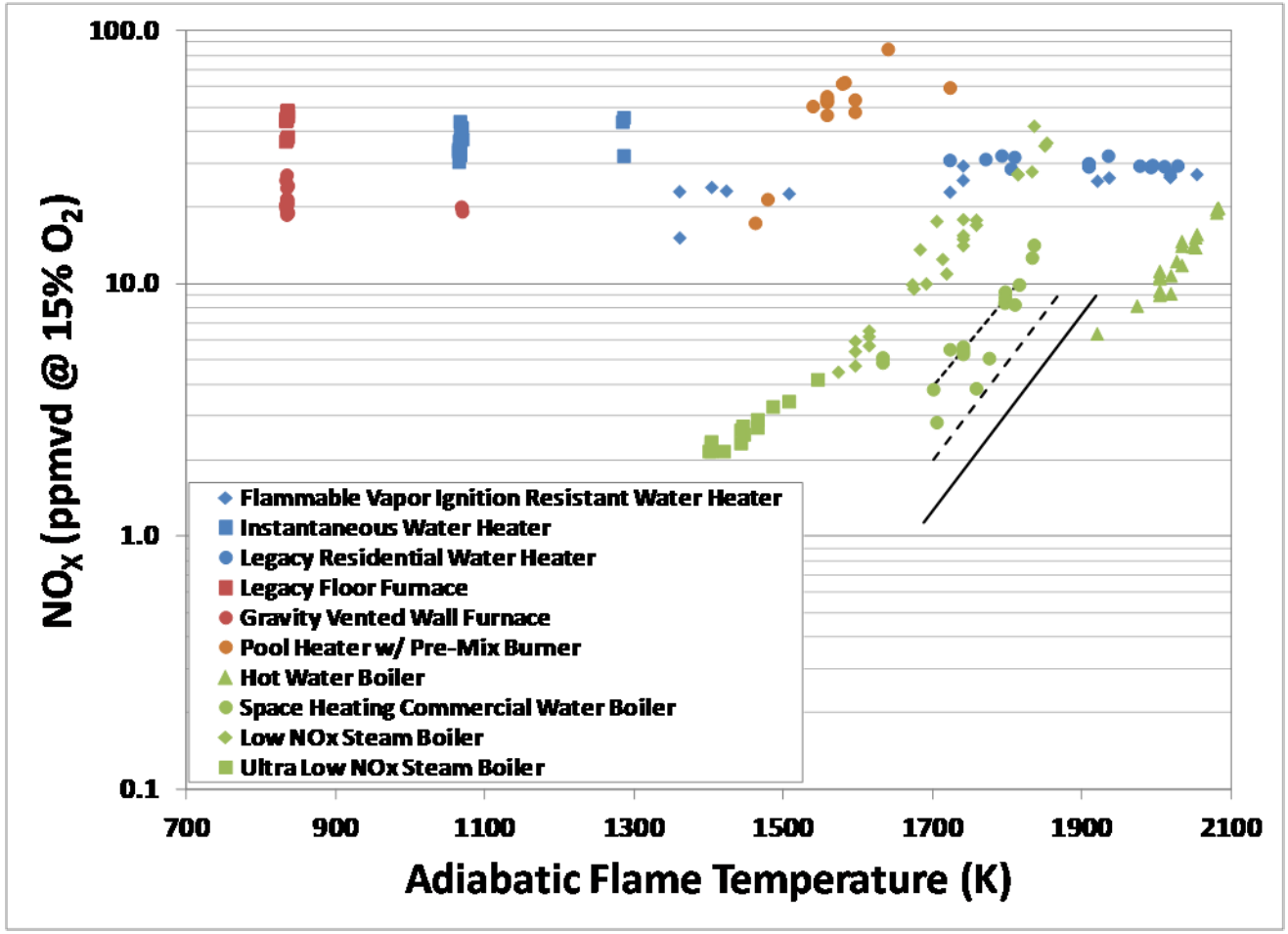
Entitlement Levels: Natural Gas

- **Perspective: Natural Gas Fired Advanced GT Combustion Technology**
  - **AFT?**
  - **Fuel Composition?**



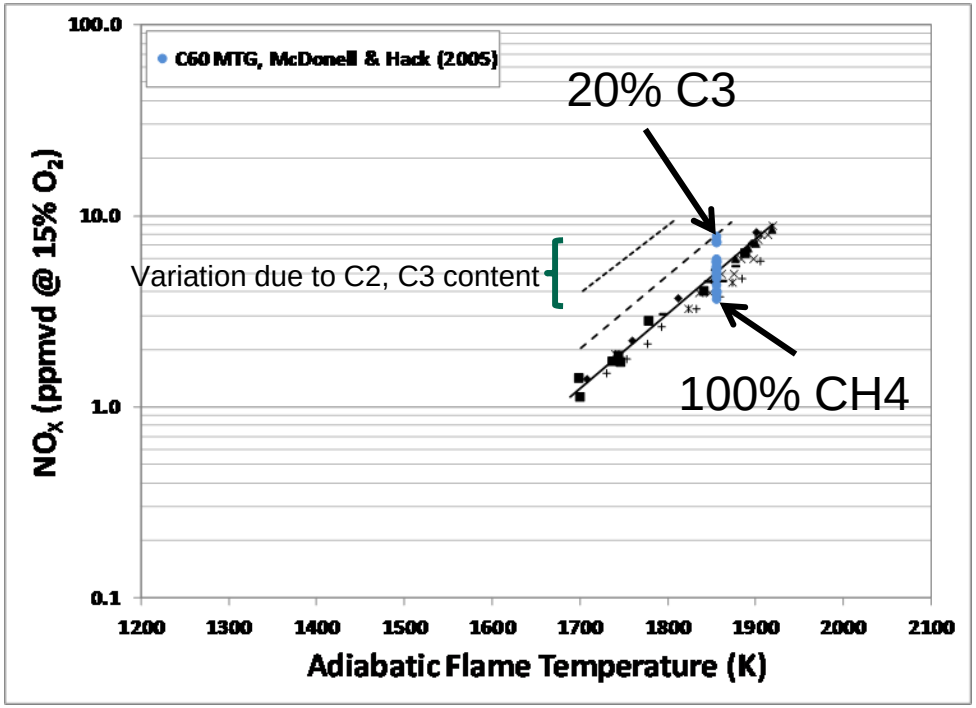
Entitlement Levels: Natural Gas

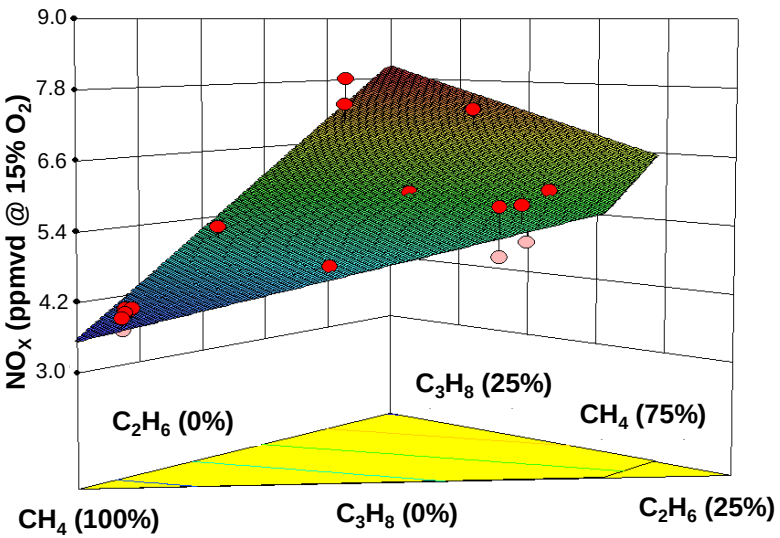
- **Perspective: Industrial Burners (SCG 2005)**



Entitlement Levels: Alkanes

- **Role of Fuel Composition?**



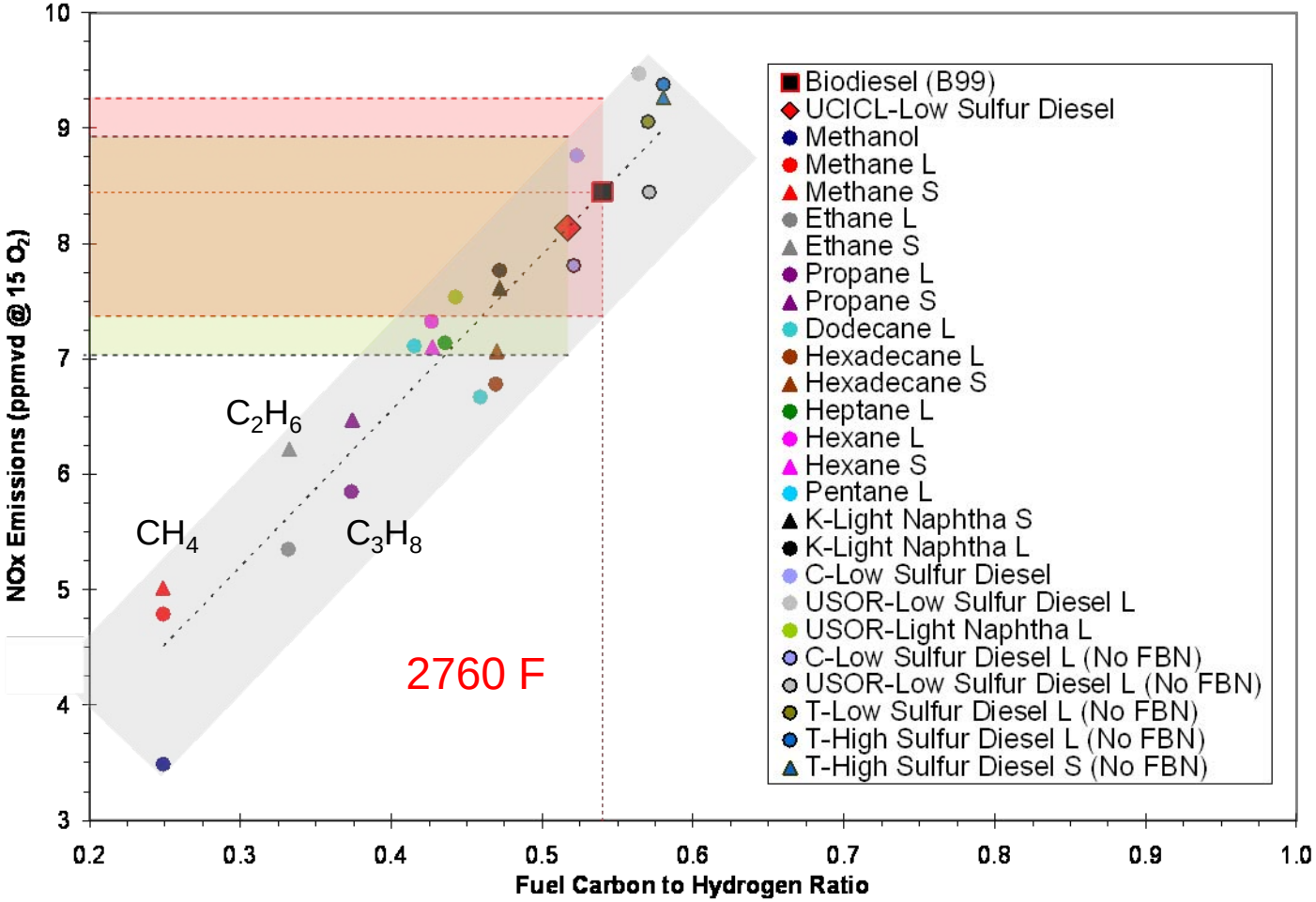


Capstone C60—meets CARB NOx emission levels→SOA Combustion

- **4:1 presure ratio, 866.5 K inlet air temperature**
- **Constant 1855 K firing temperature**
- **Propane mixtures yield highest NOx, followed by Ethane, then pure Natural Gas**

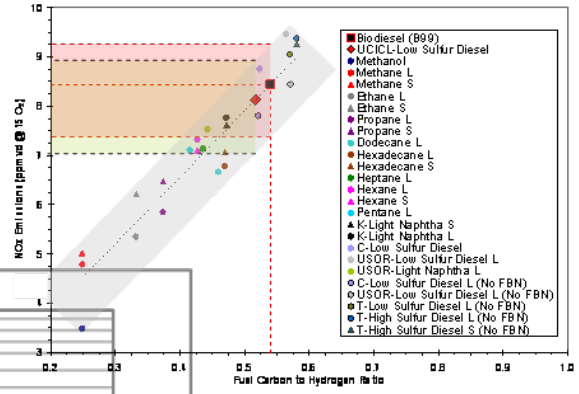
Entitlement Levels: Alkanes

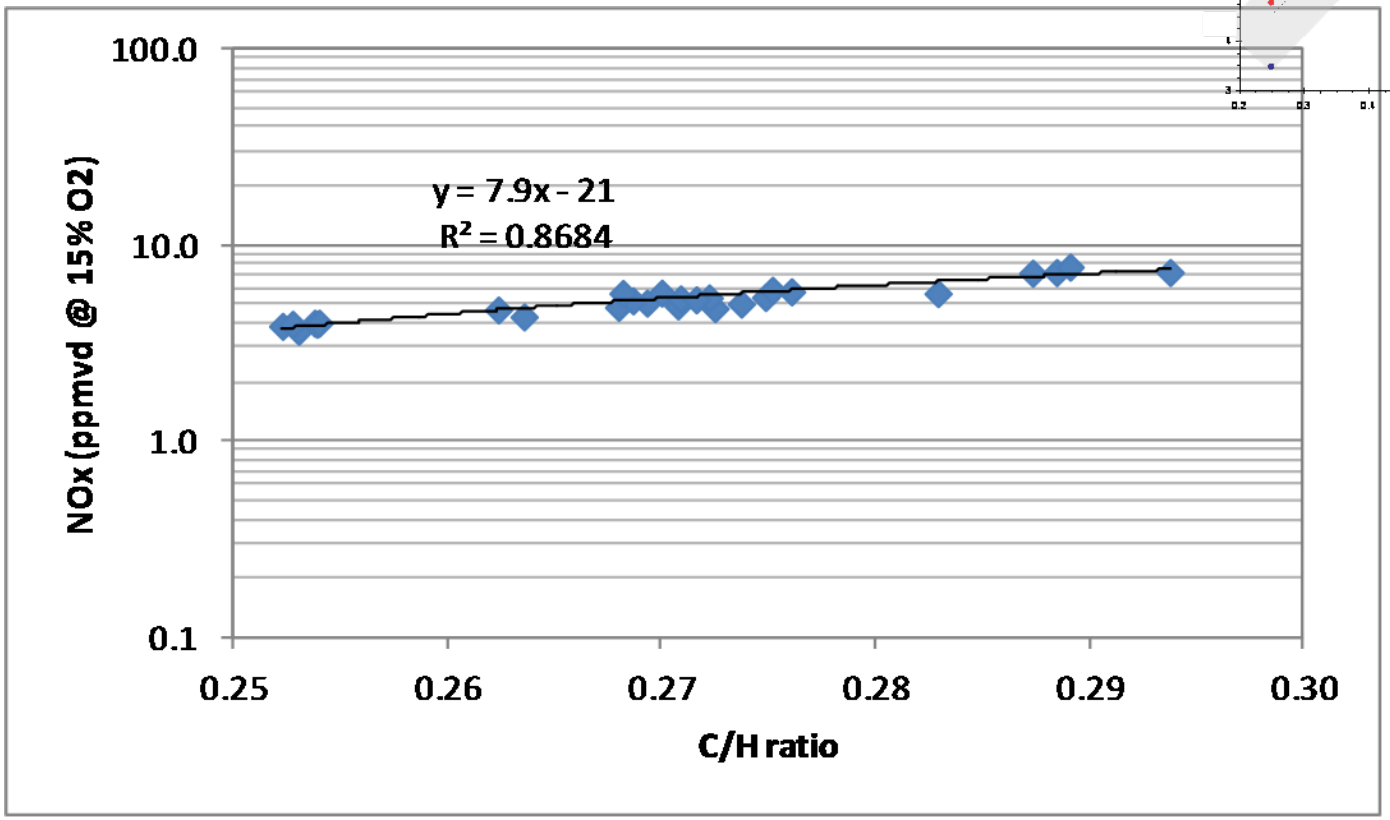
- **C:H ratio (adapted from UofW—Lee, Malte, et al.)**
  - **Fixed Firing Temperature 2760 deg F**



Entitlement Levels: Alkanes

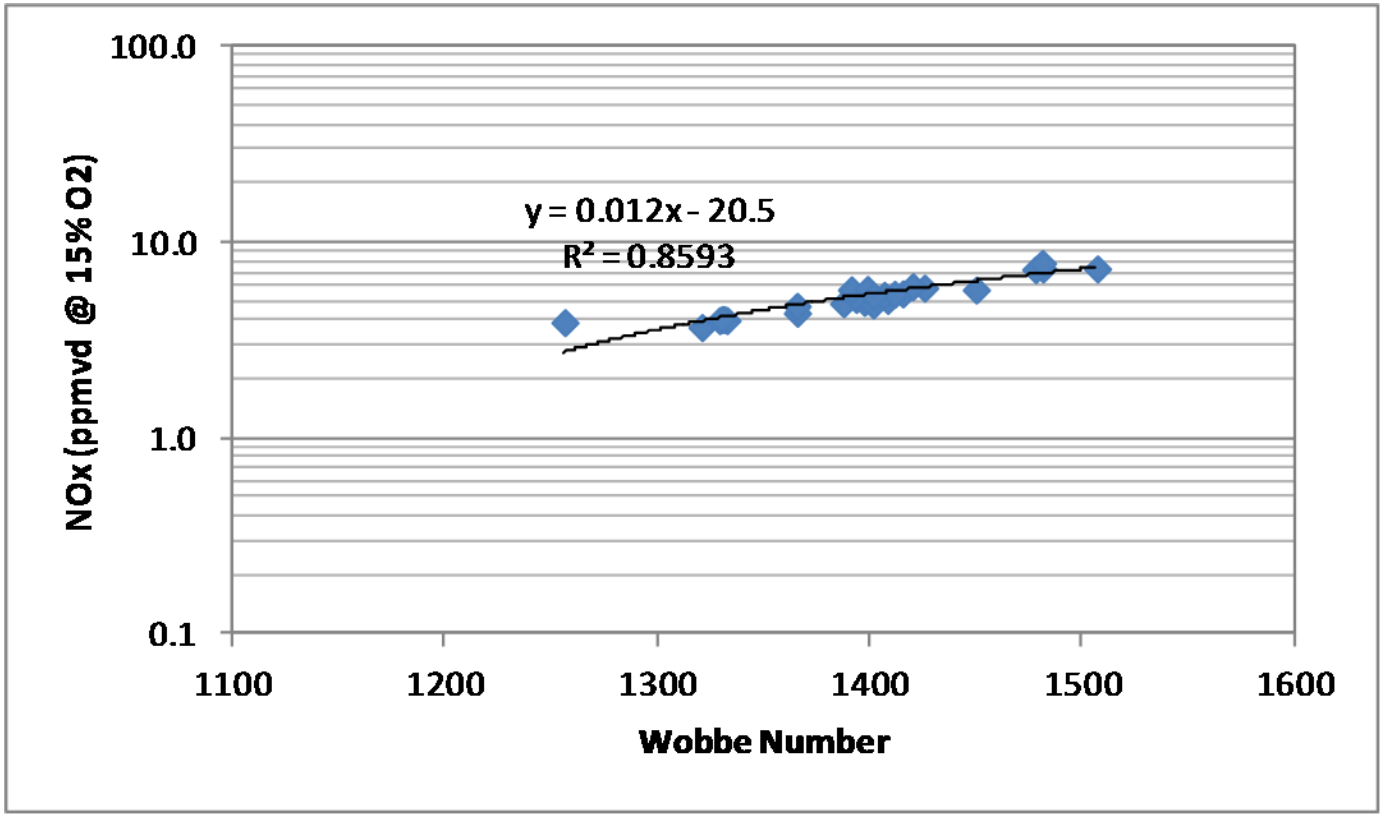
- **C-60 data: C/H modifier?**
  - **Consistent with UoW work**





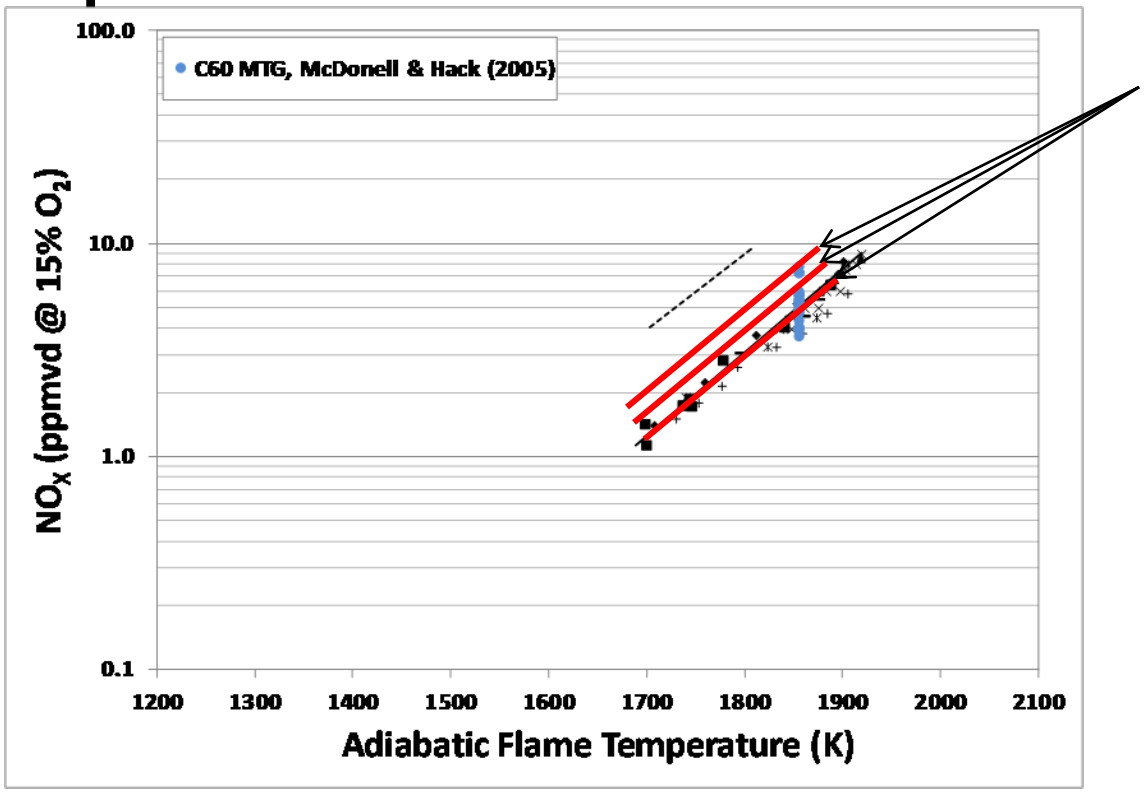
Entitlement Levels: Alkanes

- **C-60 data: Wobbe Index Modifier?**



Entitlement Levels: Alkanes

- **Modified Entitlement to account for fuel composition?**



Different C/H Ratios/ Wobbe Numbers?

Different "Entitlement" lines for C/H ratios and/or Wobbe Numbers?

- **Varying slopes? Different y-intercept?**
- **Insufficient low emissions data available (GTI?) or Task 6 (UCI Validation—C-60)**

Example Results

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  - **Autoignition Interchange Criteria**
    - **Design Guides to predict time to ignition**
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Higher Order Methodologies

- **Task 3--University of Washington**
  - **Development of Emissions Prediction Methodologies vs Fuel Composition and Type**
  - **Jet Stirred Reactor Test Bed**
    - **Mimics Gas Turbine Combustion Zone**
    - **Controlled, measured reaction temperature**
    - **1800 deg K fixed—focus on fuel composition effects**

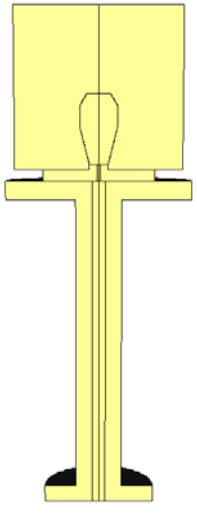
  - **Details:**
    - **Fackler, et al (2011): Experimental and Numerical Study of NOx Formation from the Lean Premixed Combustion of CH_4 Mixed with CO_2 and N_2. Paper GT2011-45090, TurboExpo 2011, June. (accepted for publication *J. Engr Gas Turbines and Power*)**

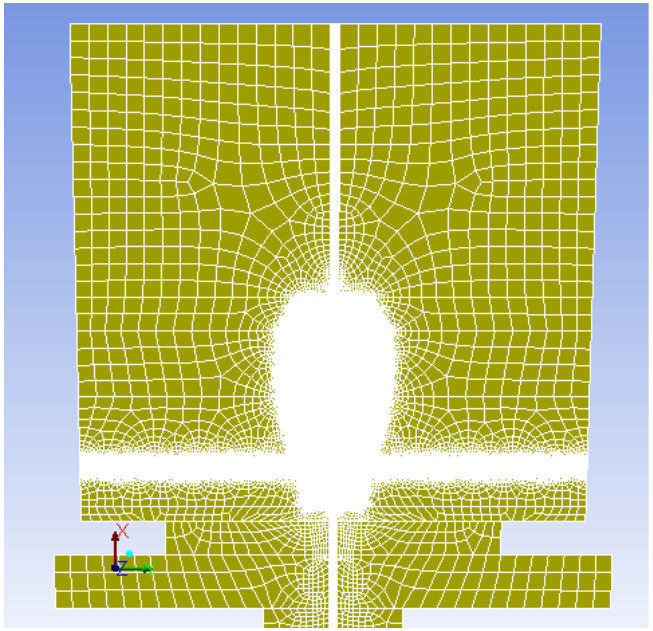
Burner Models: Two Approaches

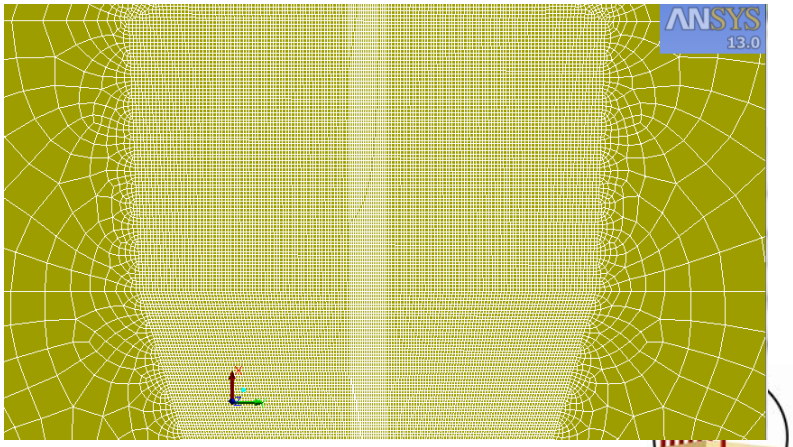
- **More sophisticated methods for evaluating impact of fuel composition on emissions**
  - **Detailed computational fluid mechanics (CFD)**
    - **Limited chemistry, used to gain insight into fluid mechanics (full H_2, truncated hydrocarbons)**
    - **Convergence in days w/reduced chemistry, months with sufficient chemistry to establish fuel impacts**
  - **Chemical Reactor Network modeling (CRN)**
    - **Reactor network designed using CFD to capture major trends**
    - **Uses detailed chemistry, including NOx**
    - **Convergence in minutes**

CRN Development

- **Step 1: Gain details about structure of flow and heat release**
  - **CFD w/limited chemistry**
  - **Measurements**
- **CFD is ubiquitous in most burner OEMs**







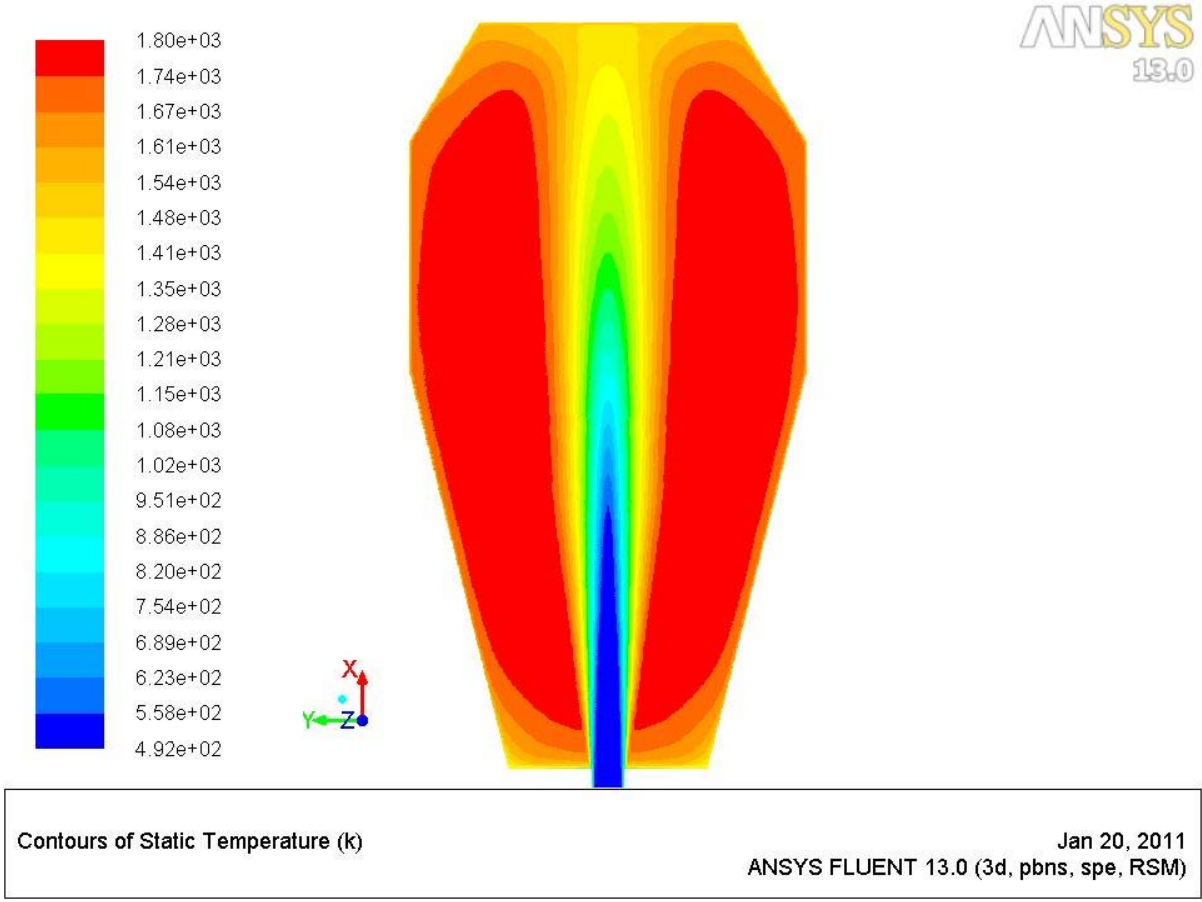
CFD: Mesh and Boundary Conditions

- 3-D CFD simulations encompassing both the solid and fluid portion of the JSR
- Structured Domain in fluid volume of about 1,000,000 cells
  - Fluid cells ~ 71% (66% in JSR chamber)
  - Solid cells ~ 29% (because of boundary)
- Refined in the fluid portion of the JSR
  - Max Cell length ~ 0.158 mm
- Natural convection and radiation at boundary, conduction in the solid
- Pressure Inlet/Outlet (Compressible)
  - Mass flow rate will adjust
  - Difference between model and experiment is less than 1%

- 2-D CFD simulations encompassing both the solid and fluid portion of the JSR
- Structured Domain in fluid volume of about 35,000 cells
- Refined in the fluid portion of the JSR
  - Max Cell length ~ 0.065 mm
- Slot flow; adjusted to give correct reactor pressure

General Flow Characteristics

- **Unlike the ideal PSR, the JSR exhibits three zone behavior:**
  - **A cold premixed jet**
  - **Flame brush around jet (for most fuels and conditions)**
  - **Surrounded by hot recirculating products**
- **Mean residence time = 3ms**
- **One large eddy turn over time is about 1 ms**
- **Average particle makes 3 eddy turnovers**

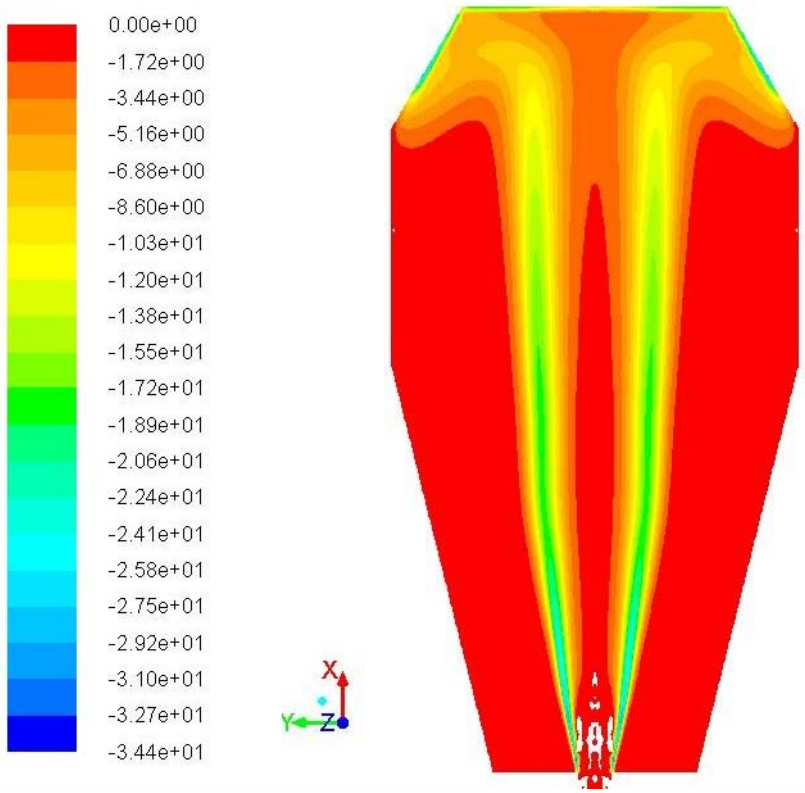


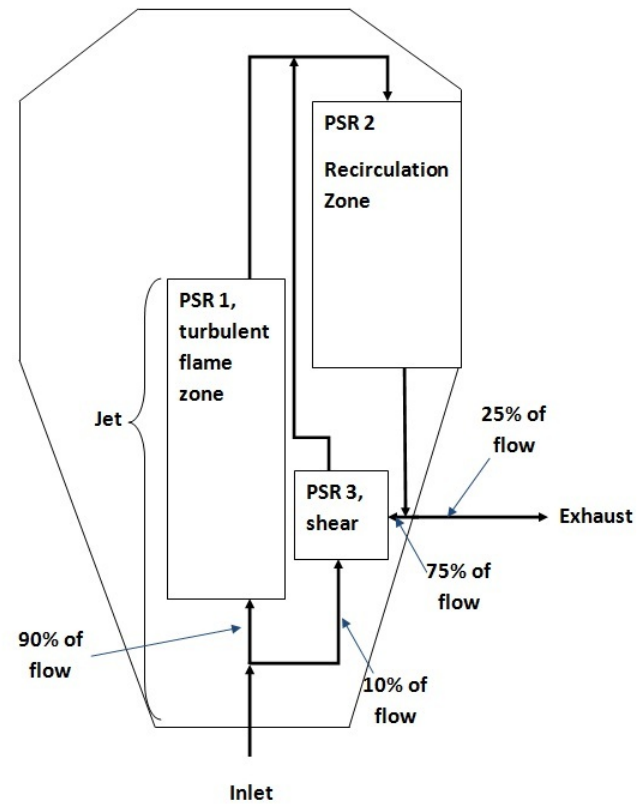
- **Noted similarity with C-60 combustion!**

CRN Development

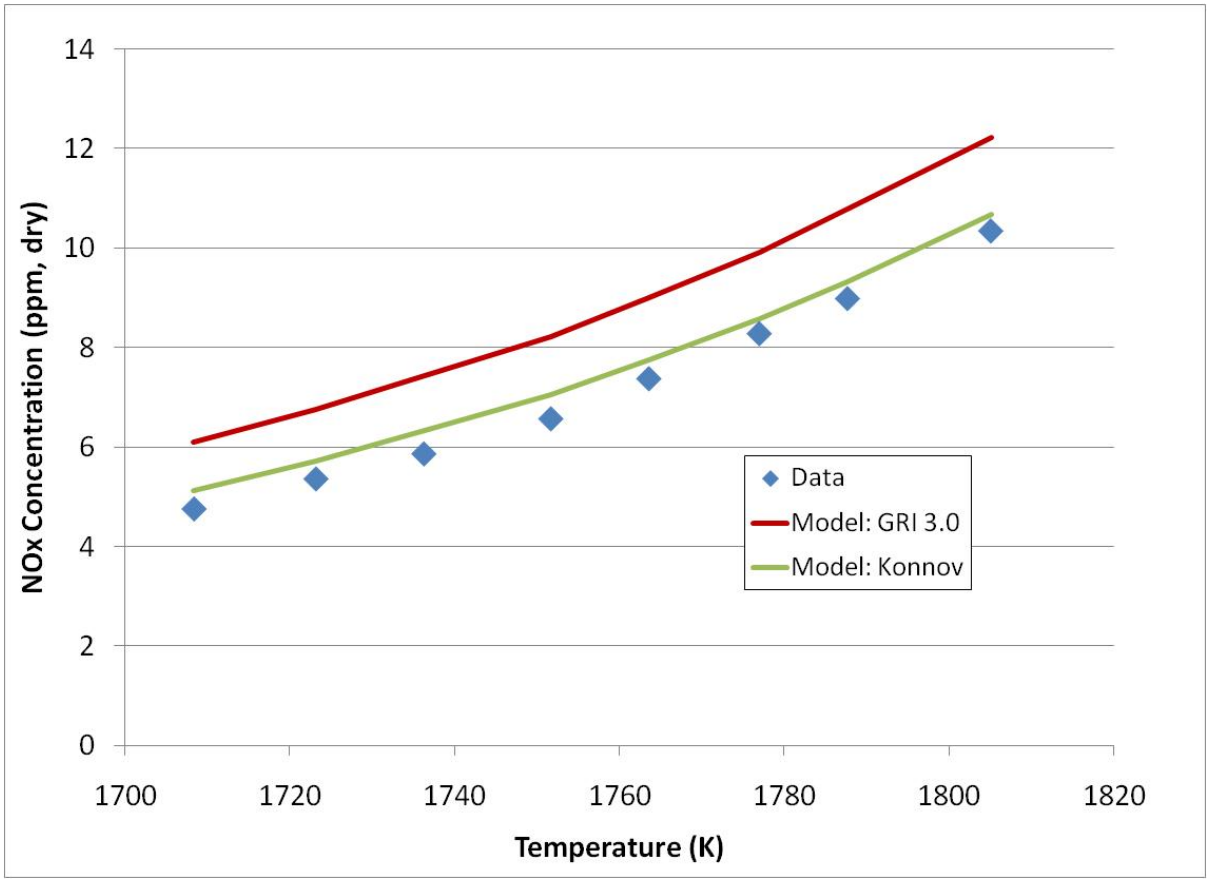
- **Step 2: Break domain into appropriate reactor(s)**

CH_4 Reaction Rate





CRN Sample Results



- **CH_4 Combustion at different temperatures**
- **Both Models display the proper trend**
- **GRI tends to slightly over predict the data**
- **Detailed Chemistry allows evaluation of NOx as a function of fuel composition**

Four NO_X Formation Pathways

- Zeldovich
  - Result of N_2 reacting with super-equilibrium concentrations of O and OH
  - Highly temperature sensitive

$$N_2 + O \rightarrow N + NO$$
$$N + O_2 \rightarrow NO + O$$
$$N + OH \rightarrow NO + H$$

- N_2O
  - Mainly a result of N_2 reacting with O and a third body
  - N_2O then reacts with O to form 2NO

$$N_2 + O + M \rightarrow N_2O + M$$
$$N_2O + O \rightarrow NO + NO$$

- Prompt
  - Initialized by N_2 reacting with CH_i radicals
  - HCN and N are quickly oxidized to NO

$$N_2 + CH \rightarrow HCN + N$$

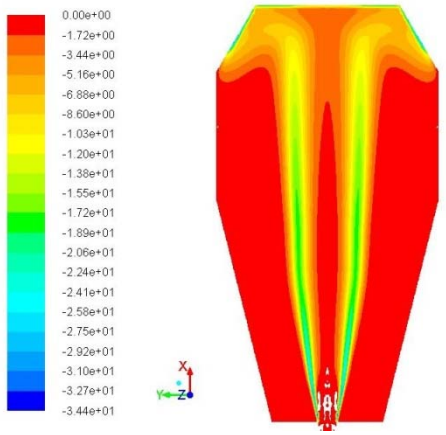
- NNH
  - Initialized by N_2 reacting with H
  - NNH reacts with O to form NO and NH which is also oxidized to NO

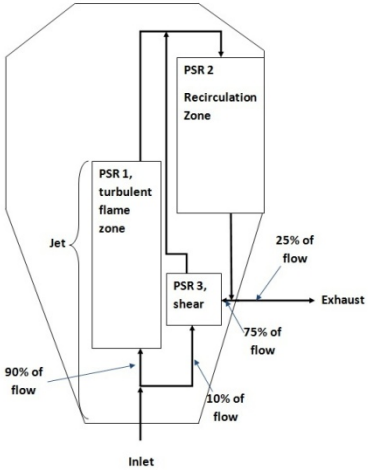
$$N_2 + H \rightarrow NNH$$
$$NNH + O \rightarrow NH + NO$$

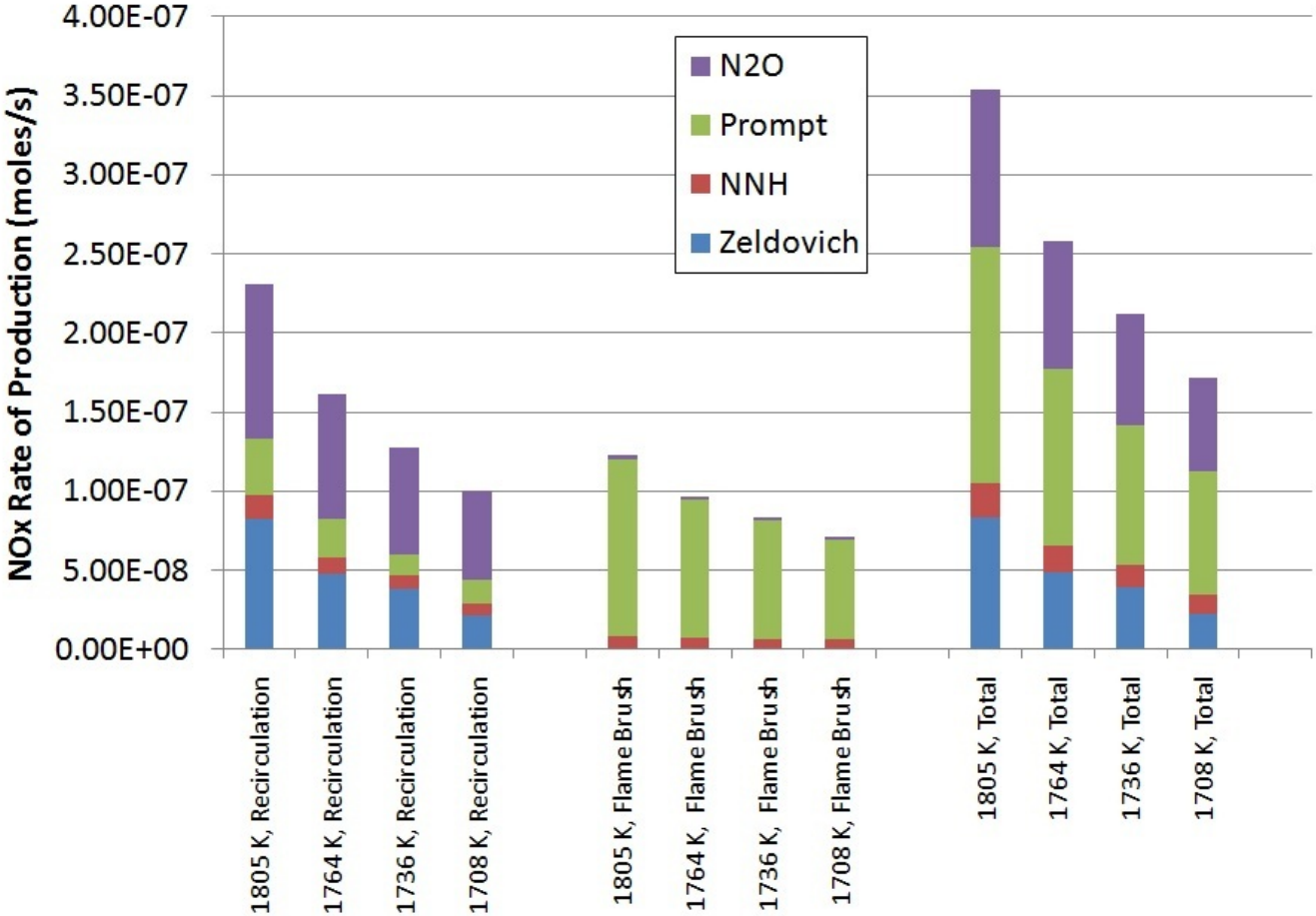
Role of each mechanism can be evaluated by crippling first reaction of each

CH_4 CRN Model

- Preliminary results suggest that the C_2H_6 and C_3H_8 in LNG increase the Prompt pathway while leaving the others unchanged. Consistent with C/H and C-60 results presented previously

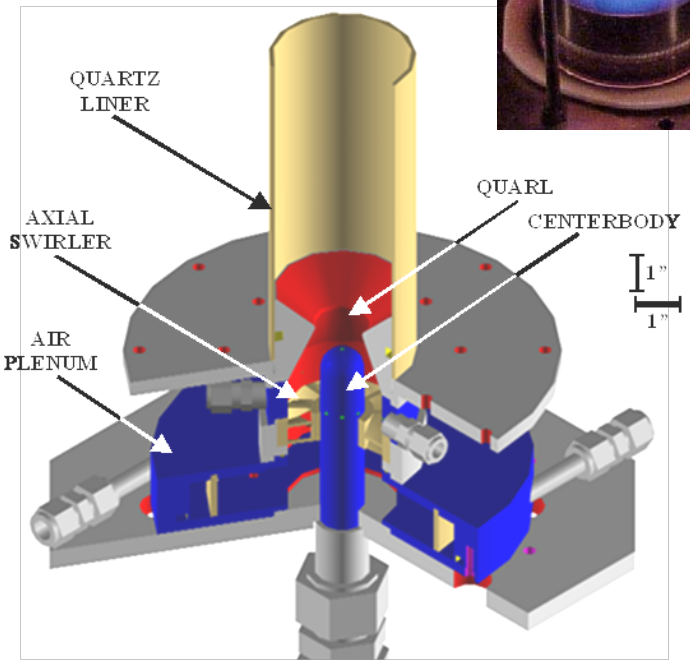






CRN Model: Next Steps

- **Validation of CRN Approach (Task 6--UCI)**
  - **CFD simulation in progress**
    - **Defines velocity and thermal fields**
  - **PIV/Imaging measurements in progress**
    - **Validate CFD/define flow**
  - **Derive CRN**
  - **Apply CRN for various fuels**
  - **Measure emissions**
  - **Measure flashback**
  - **Measure blowoff**
  - **Compare CRN emissions with measured emissions**
  - **Compare flashback & blow off w/ design guides**



High Swirl Burner—more typical of current systems

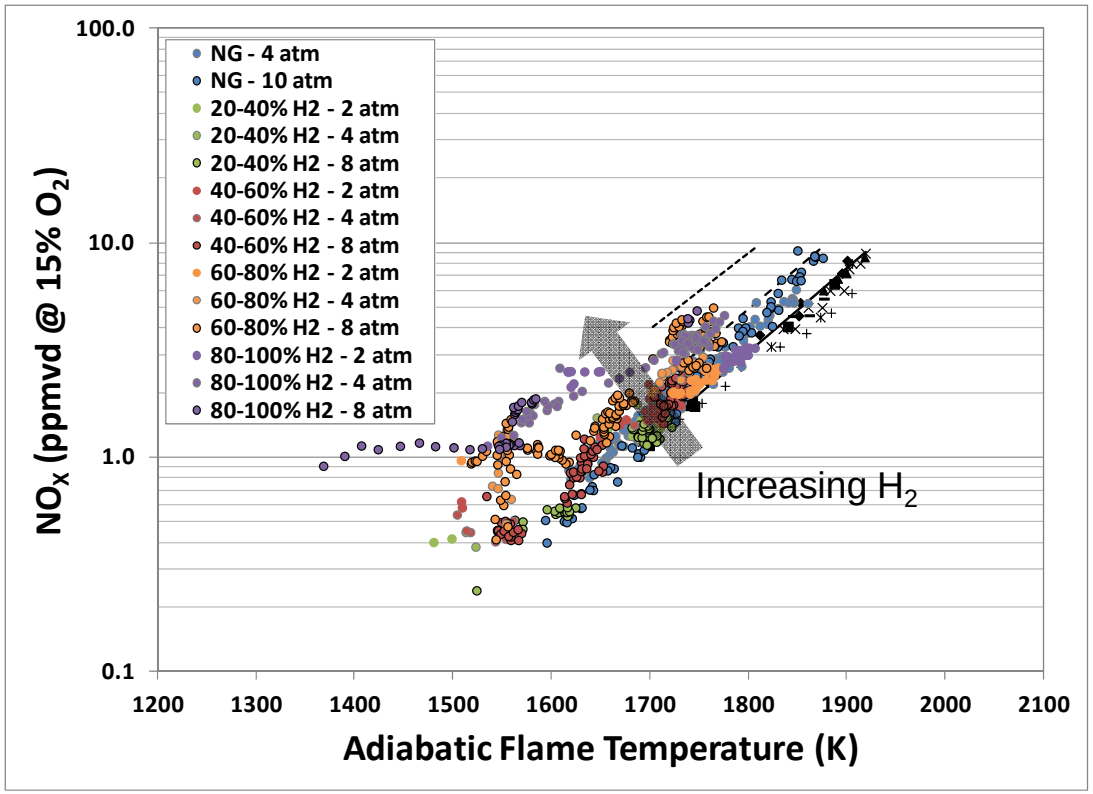
Example Results

- **Focus on Alkanes (i.e., LNG)**
  - **Autoignition Interchange Criteria**
    - **Design Guides to predict time to ignition**
      - Implications for burner/turbine premixer design
      - Implication for knock in automotive applications
  - **Fuel Interchange impacts on emissions**
    - **"Entitlement" (important relative to regulatory guidance)**
    - **Impact evaluation methodology**

- **Influence of Hydrogen Content**
  - **Emissions "entitlement"**

Entitlement Levels: Hydrogen

- **LBNL & NETL (2009)**



CH_4 and H_2 mixtures

Working pressures of 2, 4, 8, and 10 atm

91% maximum H_2 mixture at 8 atm

Reporting Emissions

- **Common practice is to report emissions on a concentration basis**
  - **Generally dry—EPA methods require water to be removed from sample because it interferes with analyzers**
    - **Analyzers generally provide direct measurement of the concentration of pollutants on a volume basis**
      - [NOx], ppm→ppm,vd
  - **Generally corrected to a fixed %O_2 level**
    - **"Dilution is not the solution to pollution"**
      - [NOx], ppm→ppm,vd→ppm,vd @ 15% O_2
  - **L&S "NO_x entitlement levels" uses ppm,vd@ 15% O_2 form**
    - **Is it appropriate for fuels other than natural gas from which it was derived?**

Reporting Emissions

- **Considerations for Fuel Composition**
  - **Consider a case with FIXED AFT = 1850 deg K**
  - **Compare results for CH_4 and H_2 combustion with 70 deg F air**
  - **1850 deg K→equivalence ratio of 0.61 for H_2/Air, 0.71 for CH_4/Air**
  - **Equilibrium Products of Combustion (99.6 + % of products)**

Species	H2/Air	CH4/Air
CO_2	0	0.069
O_2	0.071	0.055
H_2O	0.226	0.138
N_2	0.699	0.734

Reporting Emissions

- **Assume 10 ppm of NO exists in these two product streams**

Species	H2/Air	CH4/Air
CO2	0	0.069
O2	0.071	0.055
H2O	0.226	0.138
N2	0.699	0.734

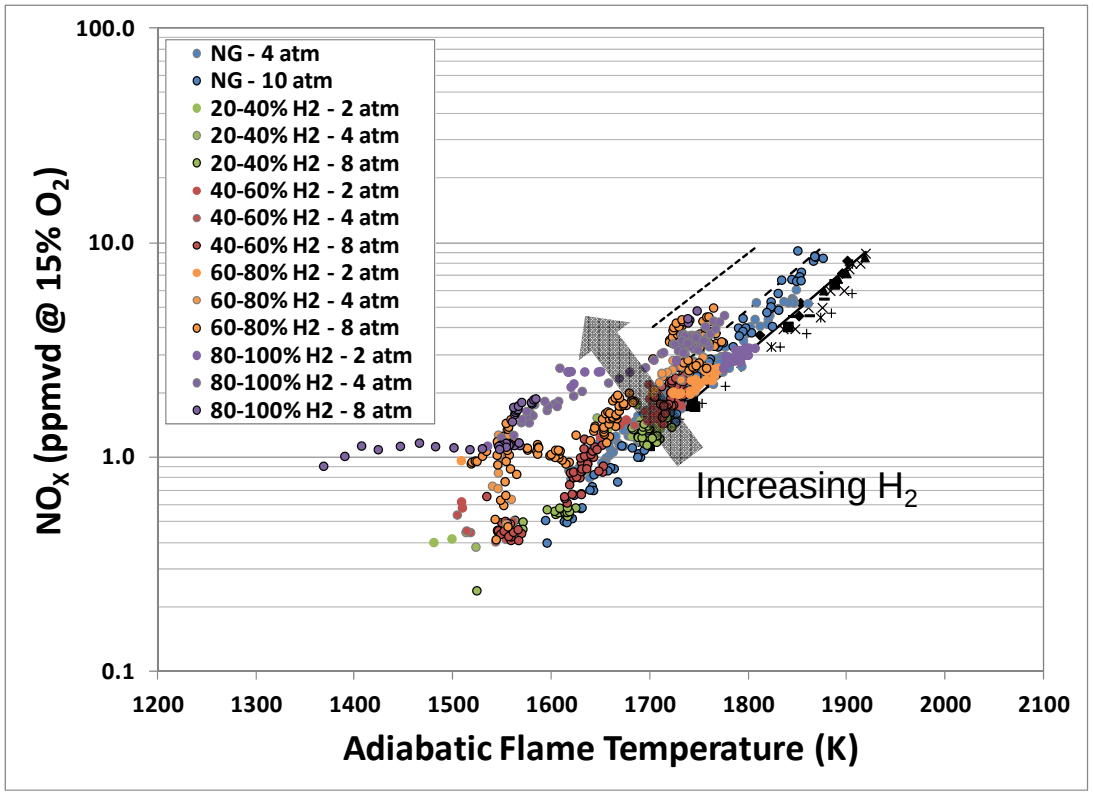
- **Concentration after correcting for water removal and correction to 15% O_2 in the exhaust**
  - **H_2/Air: 10 ppm,v → 12.94 ppm,vd → 5.58 ppm,vd @ 15% O_2**
  - **CH_4/Air: 10 ppm,v → 11.61 ppm,vd → 4.49 ppm,vd @ 15% O_2**

- **Alternatively: reporting as lb NO/MMBtu**
  - **H_2/Air: 5.58 ppm,vd @ 15% O_2 → 0.0142 lb/MMBtu**
  - **CH_4/Air: 4.49 ppm,vd @ 15% O_2 → 0.0164 lb/MMBtu**

- **H_2/Air will have 24% higher (vol.) but 13% lower (mass) NO reported all else equal**
  - **Suggests comparison on L&S ppm plot not appropriate?**

Entitlement Levels: Hydrogen

- **LBNL & NETL (2009)**



CH_4 and H_2 mixtures

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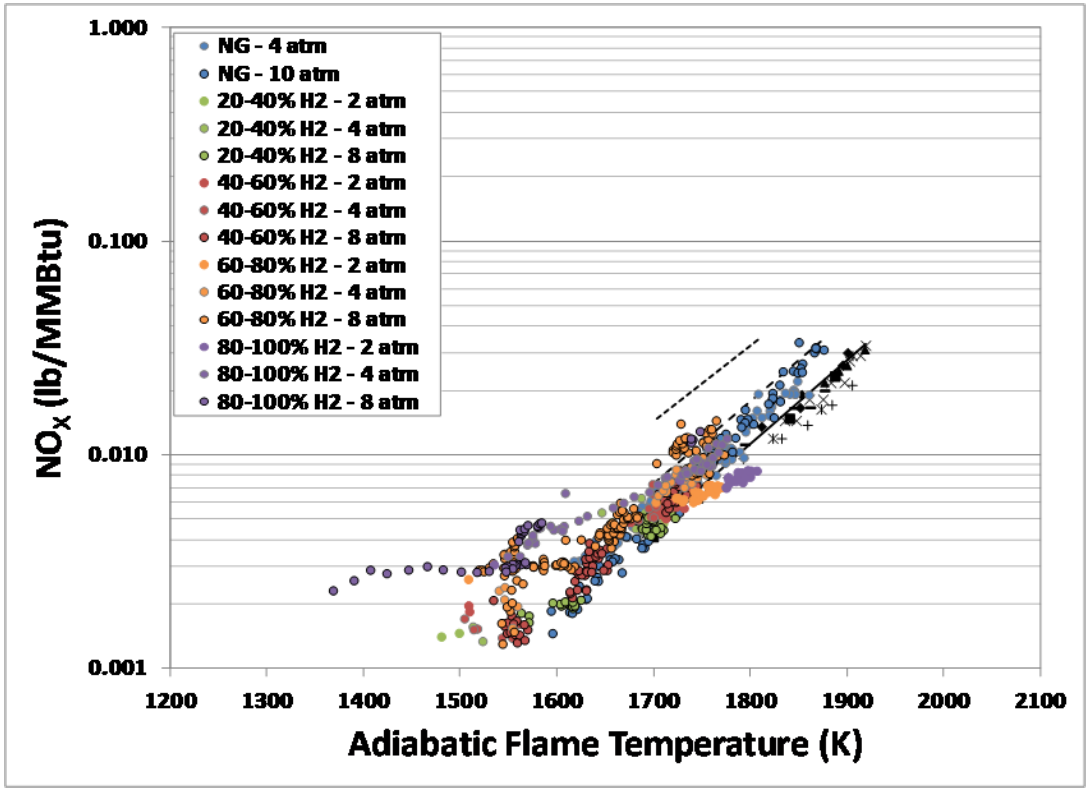
Entitlement Levels: Hydrogen

- **LBNL & NETL (2009)**



Expression on mass of NOx per MMBTU tends to collapse results for different fuels—more appropriate format for comparing fuels?

Need to examine additional data sets (H_2/CH_4 mixture emissions data in hand from PSI, LBL, Chevron, John Zink). UCI, UW data in progress

Summary

- **Focus on Alkanes (i.e., LNG)**
  - **Autoignition Interchange Criteria**
    - **Design Guides to predict time to ignition**
      - Implications for burner/turbine premixer design
      - Implication for knock in automotive applications
  - **Fuel Interchange impacts on emissions**
    - **“Entitlement” (important relative to regulatory guidance)**
    - **Impact evaluation methodology**

- **Influence of Hydrogen Content**
  - **Emissions “entitlement”**

Next Steps

- **Ignition Delay**
  - **Alkanes completed**
  - **hydrogen containing fuel measurements 75% completed**
  - **Diluted Alkanes to be done this summer**
  - **Correlation Development and validation of mechanisms**
- **Emissions**
  - **More data from advanced low emissions systems (GTI?)**
  - **Continue regression analysis for EXCEL interchange parameters**
    - **C/H, Wobbe, MN, etc.**
  - **CRN methodology validation underway**
- **Flashback/Blowoff**
  - **Data gathered for jet flame done at 1 atm (literature/new)**
  - **Measurements for low swirl flame 75% done (literature/new)**
  - **High swirl: 40% (literature/new)**
  - **Dimensionless number models being developed/evaluated**
  - **CRN methodology validation underway**

Next Steps

- **Turbulent Flame Speed (GT)**
  - **H2/CO mixtures done**
  - **Alkanes in progress**
  - **Data base to be provided for use in flashback/blowoff correlations**
    - **Interchange models include flame speed (ideally turbulent flame speed will improve generality of the models)**
    - **Evaluate performance of turbulent flame speed vs laminar in dimensionless parameter analysis**

- **Final Report Outline in development**

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