Fuels Summit 2010

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Three-Year Summary

- Extended experimental apparatuses to liquid fuels, and determined laminar flamespeeds of C4 to C8 alkanes at elevated pressures (< 20-30 atm.) using counterflow and expanding spherical flames. Further demonstrated:
  - Data consistency from different flame configurations
  - Fuel similarity
- Critically examined the issue of nonlinearity in laminar flamespeed determination from stretched flames
- Completed development of strategy for mechanism reduction; developed reduced mechanisms for several detailed mechanisms, including that of JetSurf
- Developed Chemical Explosive Mode Analysis (CEMA) for computational flame diagnostics
Outline of Presentation

- Laminar flamespeeds and chemistry (C.K. Law)
  - $C_5$ to $C_8$-alkanes
    - Laminar flamespeeds
    - Fuel similarity and internal structure
  - Iso-octane
    - Laminar flamespeeds
    - Reduced mechanism
    - Stagnation pool ignition (supported by ARO)
- Cyclo-alkanes
  - Laminar flamespeeds
- Mechanism reduction and algorithm-guided flame structure analysis
  - Chemical Explosive Mode Analysis (Tianfeng Lu)
$C_5$ to $C_8$ $n$-Alkanes

Laminar Flamespeeds and Fuel Similarity
Motivation for Present Study

- Fuel similarity demonstrated at 1 atm by Davis and Law (1998) for C4 to C7 hydrocarbons
- Ji et al. demonstrated fuel similarity for C5 to C12 at 1 atm
- Does fuel similarity still hold at elevated pressures?
  - Elevated pressures change chemical kinetics, increasing the frequency of three-body reactions
  - Relevance to practical engine conditions
Objectives

- Assess if fuel similarity still holds at elevated pressures
- Examine flame structure and assess mechanism predictions of the flamespeed
- Scrutinize data currently in the literature
Experimental Configuration

Outer Chamber

Inner Chamber
Comparison of n-Heptane

1 atm, 353K

10 atm, 353K

n-Alkane Flamespeeds (1 of 2)

n-Pentane, 353K

n-Hexane, 353K

Solid Lines: JetSurf 1.0 Mechanism
n-Alkane Flamespeeds (2 of 2)

n-Heptane, 353K

n-Octane, 353K

- Solid Lines: JetSurf 1.0 Mechanism
Comparison of $C_5$- to $C_8$-Alkanes

**Flamespeed**

**Markstein Length**
Helium-Diluted Flamespeeds

**Flamespeed**

- Fuel mixed with 15 mol % O2 / 85 mol % He
- Solid Lines: JetSurf 1.0 Mechanism

**Markstein length**

Equivalence Ratio, $\phi$ vs. Markstein Length, $L_\text{m}$ (cm)
Heat Release and Temperature Profiles

- Nearly identical heat release and temperature profiles
- Flame speed primarily depends on the adiabatic flame temperature, which is nearly identical for all fuels studied
- Temperature gradient controls heat transfer
Fuel Decomposition

Species Profiles

- $\text{C}_2\text{H}_4$
- $\text{C}_3\text{H}_6$
- $\text{CH}_4$
- $\text{C}_2\text{H}_6$

Reaction Progress

- $\text{C}_2\text{H}_6 + \text{H} \leftrightarrow \text{aC}_3\text{H}_7 + \text{H}_2$
- $\text{C}_2\text{H}_4 + (\text{H} + \text{M}) \leftrightarrow \text{C}_2\text{H}_2 + \text{H}(\text{H} + \text{M})$
- $\text{CH}_3 + (\text{H} + \text{M}) \leftrightarrow \text{CH}_2(\text{H} + \text{M})$
- $\text{C}_2\text{H}_3 + \text{H} \leftrightarrow \text{C}_2\text{H}_2 + \text{H}_2$
Radical Concentrations and Reactions

Species Profiles

Reaction Progress

![Graphs showing mole fraction and reaction progress](image)

- CO/10
- H
- O
- OH
- HO₂

- HCO+H² O ↔ CO+H₂O
- H+O₂ ↔ O+OH
- HCO+H ↔ CO+H₂
- CO+OH ↔ CO₂+H
iso-Octane

Laminar Flamespeeds, Nonpremixed Stagnation Ignition, and Reduced Mechanisms
Motivation

- Chemical kinetics of iso-octane needs to be well understood to accurately model realistic fuel combustion
  - iso-Alkanes constitute a large fraction of real fuels
  - iso-Octane and n-heptane are components of primary reference fuels (PRF)
  - iso-Octane is often included in surrogate fuel mixtures
- Kinetics needs to be scrutinized against accurate experimental measurements
  - Experimental measurements of laminar flamespeeds show discrepancies
  - Only one set of experimental measurement of the diffusive ignition temperature of iso-octane with none at elevated pressures.
- Present study: Employ three experimental facilities to measure fundamental properties of iso-octane combustion (i.e. CF and OPF for flamespeeds, stagnation pool for ignition).
Chemical Kinetic Mechanisms

Numerous mechanisms exist in the literature. Two mechanisms are widely used and have been selected for comparison in the present study:

1. Chaos et al. Primary Reference Fuel (Mech-PRF)
   - 116 Species, 754 reactions
   - Includes high temperature chemistry only

2. Lawrence Livermore National Labs (Mech-LLL)
   - 857 Species, 3606 reactions
   - Both high and low temperature chemistry included
   - Mechanism size makes even simple calculations like the laminar flamespeed time-consuming - therefore, the mechanism was first reduced.

Mechanism Reduction

- **Mech-LLL**
  - 857 species
  - 3606 reactions

- **Mech-112**
  - 112 species
  - 467 reactions

- **Mech-78**
  - 78 species
  - 158 reactions

- Directed Relational Graph Aided Sensitivity Analysis
- Quasi-Steady State Assumption Based on Computational Singular Perturbation Analysis

- **Target parameters:** auto-ignition delays, extinction residence times of PSR, and laminar flamespeeds
- **Conditions:** pressure from 1 to 40 atm, initial temperature from 600 to 1800K for auto-ignition, and equivalence ratio from 0.5 to 1.5
Flamespeed Measurement

- Both outwardly propagating flame and counterflow measurements were conducted.
Atmospheric Pressure Measurements

298K

353K

Elevated Pressure - 353K

1 atm

Flame Speed (cm/s) vs. Equivalence Ratio, $\phi$

- Present – OFF
- Present – CF
- Bradley (358K) – OPF
- Kumar (360K) – CF
- Mech-78
- Mech-112
- Mech-PRF

2 atm

Flame Speed (cm/s) vs. Equivalence Ratio, $\phi$

- Present – OFF
- Mech-78
- Mech-112
- Mech-PRF

5 atm

Flame Speed (cm/s) vs. Equivalence Ratio, $\phi$

10 atm

Flame Speed (cm/s) vs. Equivalence Ratio, $\phi$

- Jerzembeck (370K) – OPF
Disparity Coefficient

\[
\left( \frac{\partial \ln f}{\partial \ln k_i} \right)_\phi \left( 1 - \frac{k_{i,\text{Mech-PRF}}}{k_{i,\text{Mech-112}}} \right) T_{ad}(\phi)
\]

- **H2O+M<=>H+OH+M**
- **HCO+O2<=>CO+HO2**
- **HCO+CH3<=>CH4+CO**
- **HCO+OH<=>CO+H2O**
- **CO+OH<=>CO2+H**
- **CH2(s)+O2<=>CO+OH+H**
- **H+O2<=>O+OH**

Normalized Sensitivity Coefficient
Liquid Pool Ignition Experimental Setup
Comparison with Literature Data

Present measurements have been converted to global strain rate and alternate thermocouple temperature determination to allow comparison with the measurements of Seshadri et al.
Experimental data straddle between predictions using Mech-PRF and LLL.

Predictions from PRF seem to be better at higher pressures, although it only includes high-temperature chemistry.

This indicates that the dominant pathways for diffusive ignition in strained flows could be strongly affected by high temperature pathways.
Cyclo-Alkane

Flamespeeds

Cyclo-hexane
Methyl-cyclohexane
cyclo-Alkanes

cyclo-Hexane

Methyl-cycloHexane

Solid Lines: JetSurf 1.1 Mechanism
Summary on Flame Experiments and Simulation

- Combustion chamber modified allowing experimentation with moderately volatile liquid fuels
- Laminar flame speeds determined for various alkanes
- Fuel similarity for n-alkanes demonstrated for C₄ to C₈ n-alkanes at elevated pressures.
- Consistency in flame speeds determined from different flame configurations
- Reduced mechanisms of fuels derived whenever needed
- Initiated work on cyclo-alkanes, branched alkanes, and aromatics
Chemical Explosive Mode Analysis for Computational Flame Diagnostics

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Background

Rapid growth in computer power enables direct simulation of turbulent flames.
Background:
Recent Direct Numerical Simulations by Sandia

Yoo et al, 2008
3-D lifted hydrogen jet flame
1 billion grid points
3.5 million CPU hours
30TB output

Yoo et al, 2009
3-D lifted ethylene jet flame
1.3 billion grid points
14 million CPU hrs
240 TB output

Formaldehyde mass fraction, rendering by H. Yu and K. L Ma of SciDAC Ultrascale Visualization Institute

Courtesy of Ma&Yu SciDAC UltraViz Inst.
Background: Computational Flame Diagnostics

- Conventional scalars (T, species concentrations, etc.)
  - Arbitrary selection of threshold values
  - Incomplete/inconsistent information, e.g. flame front locations
  - Need human experience/interaction
- Rigorous, automatic & efficient tools needed for computational diagnostics of peta-/exa-scale simulations
Chemical Explosive Mode Analysis (CEMA)

- Governing equations for a chemically reacting flow
  \[
  \frac{Dy}{Dt} = g(y) = \omega(y) + s(y)
  \]
  \(y\): the vector of variables (e.g. species concentration and temperature)
  \(\omega\): chemical source term
  \(s\): other source terms (e.g. diffusion)

- The chemical Jacobian
  \[
  J_\omega = \frac{\partial \omega}{\partial y}
  \]

- Chemical mode
  \[
  f = b \cdot g
  \]
  \(b\): a left eigenvector of \(J_\omega\)

- Positive eigenvalue, \(\lambda_{\text{exp}}\), of \(J_\omega\) indicates chemical explosive mode (CEM)

- CEMA vs. CSP
  - CEM is chemical, CSP modes depend on diffusion
  - CEM doesn’t imply explosive CSP modes
Role of Chemical Explosive Mode in Ignition & Extinction

- CEM is a chemical property of the mixture

Explosive mode known to be important for ignition (Fotache et al, 1998, Kazakov et al, 2006)
Role of CEM in Premixed Flames

- $H_2$-air
- $P = 1$ atm
- $T_0 = 300K$

Temperature, K

$\log_{10}(1 + \lambda_{exp})$

$x, \text{cm}$
Flame Structure from CEMA

Lifted hydrogen jet into heated coflowing air

\[ \pm \log_{10} |\lambda_{\text{exp}}|, 1/s \]

- Lean front
- Rich front
- Lifting points
Damköhler Number Defined on Chemical Explosive Mode

\[ Da = \lambda_{\text{exp}} \cdot \chi^{-1} \]

- \( Da \sim 1 \),
  Premixed flames

- \( Da \gg 1 \),
  Auto-igniting
CEMA of the Lifted Ethylene Flame

Time scale

$$\text{sign}(\lambda_{\text{exp}}) \times \log_{10}(\max(1, |\lambda_{\text{exp}}|), 1/s)$$

Da

$$\text{sign}(\lambda_{\text{exp}}) \times \log_{10}(\max(1,|D_{\text{a}}|))$$
Composition of a Chemical Mode: Species & Reactions

- **Explosion Index for Species**

\[
EI = \frac{\text{diag} \left| \begin{array}{c} a_{\text{exp}} \\ b_{\text{exp}} \end{array} \right|}{\text{sum(diag} \left| \begin{array}{c} a_{\text{exp}} \\ b_{\text{exp}} \end{array} \right|)}
\]

- **Participation Index for Reactions**

\[
PI = \frac{\left| \left( b_{\text{exp}} \cdot S \right) \otimes R \right|}{\text{sum(} \left| \left( b_{\text{exp}} \cdot S \right) \otimes R \right|)}
\]

- **Correlation of species with chemical explosive mode**

- **Contribution of reactions to chemical explosive mode**

\( a \): the right eigenvector

\( S \): the stoichiometric coefficient matrix

\( R \): the vector of net rates for the reactions

\( \otimes \): element-wise multiplication
Dominant Species for Lifted H$_2$ Flame

1: O, OH
3: O, H$_2$, OH
5: O, OH
6: H

2: H
4, T
### Dominant Species/Reaction for Lifted Ethylene Flame

<table>
<thead>
<tr>
<th>Points</th>
<th>Location</th>
<th>El, Species</th>
<th>Pi, Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>x = 1.29H y = 0.99H</td>
<td>0.61, O 0.17, OH 0.13, CH2O</td>
<td>0.26, R 82: O2 + CH3 = O + CH3O 0.22, R 83: O2 + CH3 = OH + CH2O 0.18, R155: C2H4 = H2 + H2CC</td>
</tr>
<tr>
<td>2</td>
<td>x = 2.67H y = -0.70H</td>
<td>0.34, OH 0.25, CH3 0.14, O</td>
<td>0.11, R 47: O2 + HCO = HO2 + CO 0.11, R158: O + C2H4 = OH + C2H3 0.11, R 46: HCO = H + CO</td>
</tr>
<tr>
<td>3</td>
<td>x = 3.63H y = 0.30H</td>
<td>0.97, HO2</td>
<td>0.25, R139: O2 + C2H3 = O + CH2CHO 0.24, R140: O2 + C2H3 = HCO + CH2O 0.19, R168: CH3 + C2H4 = CH4 + C2H3</td>
</tr>
<tr>
<td>4</td>
<td>x = 6.33H y = -0.78H</td>
<td>0.58, T 0.12, C2H4</td>
<td>0.09, R 1: H + O2 = O + OH 0.08, R161: OH + C2H4 = H2O + C2H3 0.08, R 21: OH + HO2 = O2 + H2O 0.08, R139: O2 + C2H3 = O + CH2CHO 0.08, R 85: HO2 + CH3 = OH + CH3O 0.07, R 46: HCO = H + CO 0.06, R 47: O2 + HCO = HO2 + CO</td>
</tr>
<tr>
<td>5</td>
<td>x = 8.17H y = 2.00H</td>
<td>0.96, CO</td>
<td>0.47, R 30: OH + CO = H + CO2 0.26, R 15: H + O2 = HO2</td>
</tr>
<tr>
<td>6</td>
<td>x = 9.55H y = -0.81H</td>
<td>1.00, CH3CHO</td>
<td>0.59, R 89: CH3 + HCO = CH3CHO 0.18, R 30: OH + CO = H + CO2 0.14, R 15: H + O2 = HO2</td>
</tr>
</tbody>
</table>
CEMA vs. Conventional Scalars for Lifted Hydrogen Flame
CEMA vs. Conventional Scalars for Lifted Ethylene Flame
Summary on Computational Flame Diagnostics

- CEMA can systematically detect
  - (Partially) premixed flame fronts
  - Local ignition/extinction
  - Dominant species/reactions for the limit phenomena
- Properties of CEMA
  - CEM is a chemical property of the local mixture, not dependent on transport
  - Systematic, no arbitrary selection of threshold values, no human experience/interaction needed
  - Scalable for distributed computation (linear speedup)