Flame Kinetics of Surrogate Jet Fuel Components

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Outline of Presentation

1. Similarity of flame kinetics of large n-alkanes
2. Flame kinetics of cycloalkanes
3. PSR kinetics of ignition and extinction kinetics (T.F. Lu)
Similarity of Flame Kinetics of Large n-Alkanes
Motivation

- Fuel similarity in terms of flame speed demonstrated at 1 atm by Davis and Law (1998) for n-C4 to -C7 hydrocarbons
- Ji et al. demonstrated fuel similarity for n-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
  - High pressure relevant for practical engine conditions
  - Examine fuel similarity in the flame structure
Constant & High-Pressure Chamber for High-Pressure Flame Studies

- Unique chamber design allows well-controlled study of expanding spherical flames in constant, high-pressure (up to 60 atm.) environment.
Flame Speed Similarity of C$_5$ to C$_8$ n-Alkanes at Elevated Pressures
Similarity in Profiles of Heat Release and Temperature

- 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
Similarity in Profiles of Decomposed Fuel Species and Reactions

Species Profiles

- $C_2H_4$
- $C_3H_6$
- $CH_4$
- $C_2H_6$

Reaction Progress

- $C_3H_6 + H \leftrightarrow aC_3H_5 + H_2$
- $C_2H_3(+)M \leftrightarrow C_2H_2 + H(+)M$
- $CH_3(+)M \leftrightarrow CH_4(+)M$
- $C_2H_3 + H \leftrightarrow C_2H_2 + H_2$
Similarity in Profiles of (Small Species) Radical Concentrations and Reactions

Species Profiles

- CO/10
- HO₂
- O
- H
- OH

Reaction Progress

- HCO + H₂O ⇌ CO + H₂O
- H + O₂ ⇌ O + OH
- HCO + H ⇌ CO + H₂
- CO + OH ⇌ CO₂ + H
Interim Summary

- Experimental laminar flame speeds of C$_5$ to C$_8$ n-alkanes almost identical at atmospheric and elevated pressures

- Computation shows almost identical profiles for:
  - Concentrations of decomposed fuels species and their further reactions in the preheat zone
  - Concentrations of small molecule species and their reactions in the active reaction zone
Flame Kinetics of Cycloalkanes
Interest in Cycloalkanes

- To what extent is fuel similarity of n-alkanes carried over to other hydrocarbon fuels?
- Cycloalkanes are major components of fuel blends
- Ji et al. 2011 found: cyclohexane > n-hexane > mono-alkylated CH; difference seems to be caused by fuel cracking process

- Same trend holds at higher pressures?
- Further contrast difference between different fuels
Experimental and Calculated Flame Speeds

**CH**
- Equivalence Ratio, $\phi$
- Flame Speed (cm/sec)
- 1 atm, 2 atm, 5 atm, 10 atm
- Cyclohexane/air 353 K

**MCH**
- Equivalence Ratio, $\phi$
- Flame Speed (cm/sec)
- 1 atm, 2 atm, 5 atm, 10 atm
- Methyl-cyclohexane/air 353 K

**ECH**
- Equivalence Ratio, $\phi$
- Flame Speed (cm/sec)
- 1 atm, 2 atm, 5 atm
- Ethyl-cyclohexane/air 353 K

**20 atm**
- Equivalence Ratio, $\phi$
- Flame Speed (cm/sec)
- Cyclohexane
- Methyl-cyclohexane
- Oxidizer: 15% mol O$_2$/85% mol He 353 K, 20 atm

**Calculation:** JetSurF 2.0

**Ji et al. 2011**
Comparisons at Elevated Pressures: Experiment

cyclohexane > n-hexane > methyl-CH ≈ ethyl-CH
Comparison at Elevated Pressures: Calculation

Simulation by JetSurF 2.0 shows similar trend
Assessment of Differences

- Difference increases with pressure: 5% at 1 atm, 13% at 10 atm
Assessment of Thermal Effect

- Identical flame temperature for cyclohexane and mono-alkylated CH
- n-hexane lower by 10 K at maximum
Assessment of Thermal Effect

- Thermal effect explains the difference between n-hexane and cyclohexane at 1 atm (Ji et al.), but not at 10 atm
- Suggesting a kinetic reason
Assessment of Kinetic Effect

- Distinctive heat release profile for cyclohexane
Assessment of Kinetic Effect

- Key termination reaction for hexane and methyl-CH
  \[ aC_3H_5 + H + M \rightarrow C_3H_6 + M \]
  which increases with pressure
- Cyclohexane cracks into much more C\(_2\) and C\(_4\) than C\(_3\).
  - Dominant role of \(\beta\)-Scission
Assessment of Kinetic Effect

- Not so for methyl-CH
Interim Summary on Cycloalkanes

- Acquired flame speed data for cyclohexane, methyl-CH and ethyl-CH from 1 atm to 20 atm
- Good agreement with JetSurF 2.0 mechanism at all pressures
- Slight over-prediction of JetSurF 2.0 at 1 atm
- Revealed the trend for flame speed: cyclohexane > n-hexane > methyl-CH ≈ ethyl-CH with relative difference 5% at 1 atm, 13% at 10 atm
- Computed flame structure and sensitivity analysis reveal that cracking of cyclohexane favors C_2, C_4 over C_3 fragments
- The special feature of cyclohexane can be explained by its symmetric structure and the general applicability of $\beta$-scission rule
A PSR Study on Effects of Surrogate Fuel Composition on Ignition and Extinction

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S-Curve of PSR for Jet Fuel Surrogates (1/2)

Mechanism: JetSurF 2.0

Inlet condition:
\[ T_{in} = 1000K \]
\[ p = 10\text{atm} \]

- Large \( n \)-alkanes feature mostly identical S-curves
- Pure \( n \)-alkane, cycloalkanes, and aromatics feature different ignition and extinction states
Inlet condition:

\[ T_{in} = 1000K \]
\[ p = 10 \text{atm} \]

- Small amount of aromatics has little effects on either the ignition or the extinction states.
- Pure n-alkanes may be sufficiently good surrogates for capturing limit flame phenomena.
Controlling Reactions for Ignition/Extinction (80% n-Dodecane + 20% Toluene)

- Both ignition (high-T) and extinction are determined by reactions involving small molecules (H, CO, C1-C3)
- A “low-dimensional manifold” may exist for high-T chemistry of large hydrocarbons

![Graph showing temperature vs. residence time for n-dodecane and n-dodecane : toluene = 8:2 and 1:1 mixtures.]

**Extinction State**
- HCO+H = CO+H2
- H+O2(+M) = HO2(+M)
- H+OH+M = H2O+M
- H+O2 = O+OH
- CO+OH = CO2+H

**Ignition State**
- HO2+HO2 = O2+H2O2
- HO2+OH = H2O+O2
- C2H3+O2 = CH2CHO+O
- CH3+HO2 = CH3O+OH
- OH+OH(+M) = H2O2(+M)
- C2H4+OH = C2H3+H2O
- aC3H5+HO2 = OH+C2H3+CH2O

**Legend**
- Mixing
Interim Summary on PSR Study

- Pure components of jet fuel surrogate (e.g. n-alkanes, cyclo-alkanes, aromatics) may feature dramatically different ignition/extinction states

- Small amount of aromatics in n-alkanes has little effects on either ignition or extinction states

- Reaction pathways involving small molecules control ignition (high-T) and extinction of jet fuels

- A “low-dimensional manifold” may exist for chemistry of large molecules for ignition (high-T) and extinction