Experimental Study of the Oxidation, Ignition, and Soot Formation Characteristics of Jet Fuels

Matthew Oehlschlaeger,
Hsi-Ping Shen, Jeremy Vanderover,
Shane Daley, and Andrew Berkowitz

Mechanical and Aerospace Engineering
Rensselaer Polytechnic Institute

Sponsor: U.S. Air Force Office of Scientific Research

Period: 2/07-present
Outline

• Motivation
• Objectives
• New Shock Tube Facility
• Ignition time measurements and kinetics discussion
  – iso-octane, n-alkanes, cycloalkanes, aromatics
• Summary
Motivation

• Developing and improving combustion systems requires multi-physics models
  – One important piece of these models is the description of fuel oxidation (kinetic mechanism)

• Development of kinetic mechanisms requires validation targets from controlled experiments
  – Shock tubes, rapid compression machines, flow reactors, jet-stirred reactors, flames, etc.

• These target measurements provide valuable insight into fuel kinetics
Objectives

• Provide validation targets and kinetic insight for larger hydrocarbon fuels of relevance to jet fuels
  – Needed for the development of kinetic mechanisms and surrogate representations of jet fuels
  – Little data is available for many larger compounds

✓ Recent and current activities
  ✓ Ignition delay time measurements
    ✓ Hydrocarbon fuel components (the focus of this talk)
    ❑ Jet fuels and surrogate mixtures

• Future activities
  – Carbon monoxide measurements (additional kinetic information, particularly regarding early time oxidation in the NTC regime)
  – Soot formation
Jet fuel composition

- n-alkanes, 28%
- iso-alkanes, 29%
- cycloalkanes, 20%
- aromatics, 18%
- other, 5%
## Ignition delay studies

<table>
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<th>Fuel</th>
<th>Status of ignition exps</th>
<th>Complete</th>
<th>In progress</th>
<th>Fuel</th>
<th>Status of ignition exps</th>
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- Recent and current efforts are focused on characterizing the ignition delay of hydrocarbon components relevant to jet fuel
- In the near future investigations of jet fuels and surrogate mixtures will begin
RPI shock tube facility

- Inner diameter = 5.7 cm
- Reflected shock pressures up to 200 atm
- Initial temperatures up to 180 ºC
- Designed for kinetic studies of low vapor pressure fuels at engine-like conditions
Heated shock tube uniformity

Heated Shock Tube Temperature Profiles

- Shock tube endwall @ x = 0
- Diaphragm @ x = 411 cm

Internal Wall Temperature [°C]

Axial Position [cm]
Ignition time measurements

- Shock velocity is measured over last meter to determine endwall conditions
- Endwall ignition time measured using OH* emission
Incident shock velocity

- Attenuation requires multiple accurate velocity measurements
- Uncertainties
  - Room temperature shock tube: 1% & 1.5% in T & P respectively
  - Heated shock tube: 1.5% & 2.0% in T & P respectively

\( n\text{-decane/air, } \phi = 0.5 \)
Shock tube heated to 60°C
Reflected shock condition: 1082 K, 49.1 atm
Incident shock attenuation: 3.5%/m

![Graph showing velocity vs. axial position](image)
Shock tube non-ideal gasdynamics

- Boundary layer induced attenuation causes P & T rise over time
- To date, we have chosen to only report ignition measurements for test times shorter than ~3 ms to avoid influence from condition changes

![Graph showing signal over time with labels for pure N₂ driven and 20% N₂/He driver, initial reflected shock conditions at 961 K, 9.7 atm, and dP/dt = ~2% / ms, estimated conditions at 4 ms as 980 K, 10.5 atm.](image)
Shock tube ignition example

Toluene/air, $\phi = 1.0$
1082 K and 46.9 atm

Signal [arb. units]
Time [\(\mu\text{s}\)]

\(\tau = 757 \, \mu\text{s}\)
endwall OH* emission

sidewall pressure
Typical parameter space
- Fuel/air mixtures at $\Phi = 0.25, 0.5, \text{ and } 1.0$
- Two pressures
  (10-15 atm and 40-50 atm)
- Variable temperature range
  (limits of 700 and 1400 K)
Iso-octane: influence of diluent gas
(LLNL simulations)

- Argon mixtures have shorter (~15%) ignition times relative to N\textsubscript{2} mixtures due to lower specific heat
Iso-octane: influence of diluent gas (experiment)

- Measurements have been made for iso-octane for both Ar and N₂ bath gases
- Ar mixtures display ignition times that are 15-20% shorter than N₂ mixtures
- Mechanisms predict 15% difference
Influence of diluent

- Measured induction period heat release (pressure rise) similar to that predicted by LLNL mechanism
- Mechanism overpredicts ignition time
Iso-octane: Comparison with previous data

- Agreement with previous Aachen and Stanford data
Measurements have been made for n-heptane, n-decane, n-dodecane, and n-tetradecane at ~12 atm and ~40 atm and for \( \Phi = 0.25, 0.5, \) and 1.0 (20 data sets).

The ignition times for all alkanes are essentially the same, within measurement uncertainties, for mixtures with common carbon content (true for all conditions studied).
N-alkanes: all available data

\[ \tau \sim P^{-1} \]

\( \phi = 1.0 \) experimental studies

all data scaled to 12 atm using \( \tau \sim P^{-1} \)

- Gauthier et al., n-heptane
- Ciezki et al., n-heptane
- Zhukov et al., n-decane
- Pfahl et al., n-decane
- Kumar et al., n-decane
- Vasu et al., n-dodecane
- current study, n-heptane
- current study, n-decane
- current study, n-dodecane
- current study, n-tetradecane
- Curran et al., n-heptane, 13.5 bar
- Westbrook et al., n-tetradecane, 13.5 bar

Data bands illustrating a factor of three in ignition time

(\( \Delta \log(\tau) = +/-0.238 \))
N-alkane kinetics

Measured and predicted ignition times are essentially independent of alkane length
• High-T: all alkanes lead to similar pool of C$_3$H$_6$, C$_2$H$_4$, CH$_3$, and H; H + O$_2$ controls
• Moderate-T: all alkanes lead to similar alkenes; H$_2$O$_2$ + M controls
• Low-T: size of R does not significantly influence the rates of peroxy reactions
• Note: small increase in reaction rate in the NTC regime with increasing alkane length observed experimentally and predicted by kinetic simulations (isomerization slightly easier for longer chains)
Cycloalkanes

- Measurements have been made for five cycloalkanes at \( \sim 15 \text{ atm} \) and \( \sim 50 \text{ atm} \) and for \( \Phi = 0.25, 0.5, \) and 1.0 (28 data sets).
- Ignition times vary in the order:
  \( \text{decalin (longest } \tau \text{)} > \text{cyclopentane} > \text{methylcyclohexane} > \text{ethylcyclohexane} > \text{cyclohexane (shortest } \tau \text{)} \)
Cyclohexane and methylcyclohexane comparisons

- Cyclohexane and methylcyclohexane
  - Agreement with previous shock tube and RCM data
  - Mechanisms overpredict measured ignition times
- No previous experiments at high pressure to compare with cyclopentane, ethylcyclohexane, and decalin data
Cycloalkane reactivity: cyclopentane vs cyclohexane

Primary reaction pathways above 900-1000 K

- Cyclopentane > cyclohexane
  - Higher activation energy for ring opening (based on QC calculation)
  - Lower reactivity of $\beta$-scission products
    \[ \text{C}_2\text{H}_4 + \text{aC}_3\text{H}_5 \text{ vs } 2\text{C}_2\text{H}_4 + \text{C}_2\text{H}_3 \]

X: H, O, OH, HO$_2$
M: third body
Cycloalkane reactivity

- Methylcyclohexane $\gg$ cyclohexane
  - $\text{C}_3\text{H}_5$ and $\text{C}_4\text{H}_6$ vs $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_3$

- Ethylcyclohexane more reactive than methylcyclohexane due to secondary H-atoms

- Decalin leads to less reactive aromatics (benzene, toluene, xylene, styrene, ethylbenzene), Violi and co-workers (UMich)
  - Least reactive compound studied
• Measurements have been made for five aromatics at ~12 atm and ~40 atm and for Φ = 0.5 and 1.0 (20 data sets)
• Ignition times vary in the order:
  Toluene ≈ p-xylene ≈ m-xylene > o-xylene > ethylbenzene
The LLNL group has revisited their toluene mechanism. Updated mechanism provides fairly accurate predictions of RPI shock tube and Case Western RCM data when heat loss is accounted for in RCM simulations.
Comparison with previous o-xylene and ethylbenzene RCM measurements

- Extrapolation of RPI data to lower temperatures shows intersection with Roubaud et al. (Lille) RCM data
- o-xylene RCM data shows NTC, ethylbenzene does not
- No previous data for m- and p-xylene for comparison
  - Lille group observed no ignition in RCM for $T < 900\, \text{K}$
Aromatic kinetics: toluene vs ethylbenzene

Toluene >> ethylbenzene
- Weaker C-C bond in ethylbenzene side chain
- Secondary H-atoms in ethylbenzene side chain
- Ethylbenzene is consumed more rapidly
- Toluene exclusively yields stable benzyl
- Ethylbenzene can yield stable $\text{C}_6\text{H}_5\text{CHCH}_3$ and more reactive $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$ radicals
Aromatic kinetics: xylenes

p-xylene \( \approx \) m-xylene > o-xylene

- o-xylene is slightly more reactive due to possible RO \(_2\) isomerization due to the proximity of the methyl side chains
- o-xylene is the only xylene to exhibit NTC behavior
Summary

• A new shock tube has been constructed for the kinetic study of low-vapor pressure fuels and fuel components at elevated pressures

• The ignition of several larger hydrocarbons of relevance to jet fuel have been investigated
  – Many new targets for kinetic modeling efforts are available
  – Diluent gas has a 15-20% influence on ignition for larger hydrocarbons
  – Larger n-alkanes display ignition times essentially independent of chain length for mixtures with common carbon content
  – The influence of structure on reactivity has been quantified for cycloalkanes and aromatics

• Near term investigations:  
  – Ignition of the diesel cetane reference fuels  
  – Ignition of jet fuel surrogates and jet fuels (JP-8 and Jet A)

• Longer term investigations:  
  – New kinetic targets including CO concentration measurements  
  – Soot formation studies
Publications

• H.-P. S. Shen and M.A. Oehlschlaeger, “The Ignition of C\textsubscript{8}H\textsubscript{10} Aromatics at Elevated Pressures,” submitted.


