Shock Tube Studies of Liquid Fuel Combustion Kinetics

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Objective:
Improve knowledge of combustion kinetics of vaporized liquid fuels relevant to the Army – through use of advanced shock tube and optical diagnostics

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Outline of Topics

1. Development of second-generation aerosol shock tube and its application to *n-dodecane* and *diesel* ignition

2. Ignition measurements of cyclic jet fuel surrogate components: *toluene* and *methylcyclohexane (MCH)*

3. Extension of the operating regime and capabilities of conventional shock tubes

4. Successful resolution of apparent discrepancy in low-T *propane* ignition delay times
Stanford Shock Tube & Laser Facilities

- Shock Tubes (4)
  - Large Diameter Tubes (15 cm and 14 cm)
  - High Pressure Tube (5 cm) heatable to 150°C
  - Aerosol Tube (11 cm)
- Optical Diagnostics
  - Absorption (VUV, UV, Vis, Near-IR, Mid-IR)
  - Kinetic Spectrograph (200-300nm)
  - Emission (UV, Vis, IR)
  - ARAS (H/O/C/N-atom detection)
- Supporting Equipment
  - Gas Chromatography for in situ Fuel Analysis
  - Excimer Photolysis for Radical Production
First-generation aerosol shock tube (AST 1)
- Turbulence-based filling method – some limitations on fuel loading range, uniformity and reproducibility

Second-generation aerosol shock tube (AST 2)
- New plug-flow-based aerosol delivery system allows partial ST filling
- Improved spatial uniformity of the aerosol by pre-mixing test mixture
- Greater range of aerosol (i.e. fuel) loadings

Recent work
- Fuel 1: N-Dodecane
- Fuel 2: Diesel (DF-2)
- New aerosol loading scheme uses two large ST gate valves, mixing plenum and dump tank; plug flow loading
- Laser diagnostics (UV to MIR) provide fuel loading, uniformity measure, and species concentration time-histories
Fuel: N-Dodecane
Ignition Delay Time Measurements

$C_{12}H_{26}/21\%\ O_2/Ar, \phi=0.5, \ 5.5\ atm$

- Quiescent shock tube behavior, similar to conventional gas-phase ST
- Low-scatter ignition delay time data
- Wide range of fuel loading ($\phi = 0.3\ to\ 1.5$ in equivalent air)
Fuel: N-Dodecane
Comparison with JetSurF Model

- JetSurF model predictions are only in “general agreement” with high-P, low-T ignition delay time data.
- Further work needed to expand range of data (P,T,Φ).

- AST 2 can provide unique vapor-phase data for low-vapor-pressure fuels in support of mechanism development and validation.
Fuel: Diesel (DF-2)
Ignition Delay Time Measurements

- New diesel ignition data (domestic DF-2, C.I.=55) in excellent agreement with previous Stanford study

- Low scatter measurements allow better quantification of ignition time variation with fuel variation (e.g. composition, Cetane Index)

- Next Step: - acquire data over wider range of conditions (T,P, mixture, $\Phi$)
  - investigate jet fuel surrogates (including bio-derived fuels)
Fuel: Diesel (DF-2)
First AST 2 Application of Multi-Species Laser Absorption Strategy

Multi-species laser absorption measurements provide new chemical kinetic targets for diesel surrogate comparison.

Multi-Wavelength Diagnostics:
- 650 nm: droplet extinction
- 3.39 µm: fuel concentration
- 10.6 µm: ethylene

Multi-species data provides time histories for fuel decomposition and stable intermediates (C₂H₄)

Reflected Shock Conditions: 1092K, 7.6 atm, 0.19% Diesel (DF-2), 21% O₂
High-quality ignition and species data needed for primary surrogate jet fuel components:
- paraffins (n-dodecane)
- cyclo-paraffins (methylcyclohexane/MCH)
- aromatics (toluene)

Critical need for low-intermediate T data

Current targets:
- **MCH**: 60 atm, 700-1100 K
- **Toluene**: need to resolve ST/RCM ignition time differences near 1000K
Ignition Measurements of Jet Fuel Surrogate Components: Toluene

- Development/refinement of surrogate jet fuel mechanisms requires reliable ignition data for toluene at engine-relevant conditions.

- **The Problem:** Recent ST and RCM studies of toluene ignition show differing trends at intermediate temperatures (900-1200 K) and high pressures (near 50 atm).

- **The Need:** Establish reliable data base for $\tau_{\text{ign}}$, especially at $T < 1050K$.

![Graph showing ignition delay time vs. 1000/T for Toluene/Air at 50 atm, $\phi = 1$](image-url)
New Shock Tube Ignition Delay Time Measurements: Toluene

- To address this discrepancy we have measured ignition delay times for toluene/air mixtures $\phi = 1.0$, 50 atm, 966-1211 K

- New measurements in good agreement with the previous Stanford study (Davidson 2005)

- Some variation in pressure time-histories with different fuel loading protocol, but no difference in ignition times

- New data also consistent with work by Shen (except for their two lowest T pts)
Toluene Ignition Delay Time Measurements: Comparison with Models

- General agreement with Andrae et al. (2008) model
- Shorter experimental times than predicted by Sivaramakrishnan (2005), but mechanism employs older rates for key reactions → Stanford Modified Model

- Stanford Modified Model uses updated rates for:
  
  \[
  \begin{align*}
  \text{H}+\text{O}_2 &= \text{O}+\text{OH} \quad (\text{GRI}) \\
  \text{Tol}+\text{H} &= \text{C}_6\text{H}_5\text{CH}_3 \quad (\text{Baulch}) \\
  \text{Tol}+\text{H} &= \text{C}_6\text{H}_5\text{CH}_2+\text{H}_2 \quad (\text{Stanford}) \\
  \text{Tol}+\text{H} &= \text{C}_6\text{H}_6+\text{CH}_3 \quad (\text{Baulch}) \\
  \text{Tol}+\text{O}_2 &= \text{C}_6\text{H}_5\text{CH}_2+\text{HO}_2 \quad (\text{Stanford}) \\
  \text{Tol}+\text{OH} &= \text{C}_6\text{H}_5\text{CH}_2+\text{H}_2\text{O} \quad (\text{Seta}) \\
  \text{Benzyl+} \text{C}_6\text{H}_5\text{CHO} &= \text{Tol}+\text{C}_6\text{H}_5\text{CO} \quad (\text{Bounaceur})
  \end{align*}
  \]

- Good agreement with Stanford Modified Model
- Next step: acquire data at lower temperatures (<1000 K) to guide model development

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**Toluene/Air**

50 atm, \( \phi = 1 \)

![Graph showing ignition delay time vs. temperature](image.png)

- 1000/T, [1/K]
- Ignition Delay Time, [\( \mu s \)]

- Andrae (2008)
- Sivaramakrishnan (2005)
- All Experiments Stanford & Shen et al.
- Stanford Modified Model (2009)
Cyclo-alkane (naphthenes) are important chemical class present in jet fuel; ignition time and species data needed for this component

Current study provides extended temperature and pressure range of data (P=1.5, 20 and 45 atm)

20 atm shock tube measurements appear to extrapolate smoothly to RCM measurements

Next Step: Testing and refinement of multi-component surrogate and models
High-quality ignition and some species time-history data now available for surrogate jet fuel components:

- paraffins (n-dodecane)
- cyclo-paraffins (methylcyclohexane/MCH)
- aromatics (toluene)

Next Steps:

- Low-T data needed for toluene
- Additional species time-history data needed for all components (especially at low T)
Topic 3: Extension of Conventional Shock Tube Capabilities

- Opportunities/Needs to extend/improve shock tube operating regime

- Stanford strategy:
  A. Extend test time using tailored gases and longer driver
  B. Use driver inserts to correct for $dP/dt$ during RS experiments
  C. Measure T directly using WMS CO$_2$ laser absorption
  D. Use CHEMShock gasdynamic model to correct for changing test conditions
Strategy A: Use Driver Extension & Tailored Mixtures to Extend Test Time

Motivation

- Critical need to overlap ST and RCM test times to resolve $\tau_{\text{ign}}$ modeling differences
- Have achieved > 40 ms!

Shock Tube with Driver Extension

(Facility modifications funded by ARO)
Strategy B: Use Driver Inserts to Improve Uniformity of Reflected Shock Test Conditions

The Problem: Boundary layers and attenuation of $V_S$ cause slow variations in $P_5$, $T_5$ with time

The Solution:
1. Driver inserts: compensates for non-ideal variation in pressure ($dP/dt$)
2. Confirm uniformity with new sensitive $T$ diagnostic

![Graph showing pressure variations with time for different conditions](image-url)
Strategy C: Confirm Uniformity using New High-Sensitivity T Diagnostic

- Direct measurement of T using wavelength modulation spectroscopy (WMS) of CO$_2$ at 2.7$\mu$m provides validation of highly uniform temperature over long test times ($\Delta T < \pm 3K$)

(T-diagnostic developed under AFOSR support)
Strategy D: Application of new reacting flow model: CHEMSHOCK

- Testing/validation of new high-fidelity reaction mechanisms with shock tube data demands both high-quality data and more accurate shock tube reactive gasdynamic models

➤ Improved model, CHEMSHOCK
- Uses CHEMKIN plus measured pressure instead of using traditional assumption of constant U,V
- Enable simulation of the temporal evolution of T and species concentrations behind reflected shock waves with chemical reaction and energy release
- Demonstrated successfully with low T ignition of hydrogen and propane
- Work in progress to extend CHEMSHOCK to allow simulation of the temporal and spatial variation of non-uniform (1-D) reflected-shock flowfields, including facility effects, as well as, chemical energy release
Low T propane ignition time data for ST and RCM both inconsistent with const. U,V

Herzler (2004) and Petersen (2007) show strong “NTC-type” behavior below 1000 K

Stanford strategy: measure propane ignition times at 6 & 60 atm using new ST techniques and interpret using CHEMSHOCK model
Use of Driver Inserts to Maintain Uniform P and T during Reflected Shock Wave Experiments: 6 atm

Propane Ignition: Low P

Experiments performed with and without driver inserts
- Without driver insert: $dP/dt = 1\%-2\%/ms$ (requires CHEMSHOCK model)
- With driver inserts: $dP/dt = \sim0%/ms$ (can use traditional constant U,V model)

Primary conclusion: Same mechanism (Curran et al. 2008) successfully simulates all low P data! No discrepancy between detailed propane mechanisms and low T ST data.

Curran et al. (2008) Model

0.8% Propane/ O$_2$/ Ar
$\phi = 0.5, 6$ atm
Future Work

- Ignition chemistry at low temperatures (NTC): Species time-histories and ignition delay times
  - Fuels: Toluene, n-Dodecane
  - Species Monitored: OH, C₂H₄, H₂O, CO₂, fuel, benzyl

- Application of AST 2: Practical, Synthetic and Bio-derived Jet Fuels
  - Fuels: S-8, Large (bio-oil derived) Methyl Esters
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- Visit Stanford website http://hanson.stanford.edu/ for

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