In-situ Measurement of Radical and Stable Species Using Absorption Spectroscopy

AFOSR BRI Review
December 4, 2013

Daanish Maqbool and Christopher Cadou
Department of Aerospace Engineering
University of Maryland
The ‘Real’ Problem

Overall Objective: Learn how to exploit endothermic reactions associated with the decomposition of a liquid hydrocarbon fuel to cool components of high speed engines without fouling due to coking (pyrolysis).
Model Problem To Be Studied

• Fuel simulant: Dilute mixtures of \( C_{12}H_{26} \) (Dodecane) and \( N_2 \)
  - \( n_{C_{12}H_{26}}/n_{N_2} \sim 0.02 \)
• Use absorption spectroscopy to measure:
  - Decomposition product concentration as function of \( x \).
  - Gas temperature profile normal to surface (wall heat flux)
• Initially consider case where \( T_{\text{fuel}} = T_{\text{wall}} \)
• Nominal Conditions: up to 1100K; 50 atm (supercritical)
• Principal governing parameter: Peclet number (diffusion)
  - Target: \( 0.1 < \text{Pe} < 100 \)
Suitability of Test Conditions

Appears possible to simulate ‘relevant’ conditions.
Micro-channel Diagnostics

• Objectives:
  – Measure decomposition products in somewhat more realistic flow environments where conjugate heat transfer is important.
  – Measure gas temperature gradient perpendicular to wall.
  – Provide data for model validation.

• Approach: Absorption spectroscopy in an optically accessible micro-channel reactor.
  – Infrared CH₄, C₂H₂, C₂H₄, C₂H₆ (major species)
    • Fourier Transform Infrared Spectrometer (FTIR)
  – Ultraviolet CH₃*, C₃H₃* (radical species)
    • Tunable laser
Challenges

• Achieving optical access
  – Form channel walls with optical materials
  – Use optical fiber beam guides (water cooled if necessary).
  – ‘Pattern’ catalyst support to provide optical access.

• Pressure broadening of major species spectra obscures IR spectra of radical species at 50 atm.
  – Both IR and UV absorption measurements are necessary.

• Generating CH$_3$ and C$_3$H$_3$ for calibration
Previous Work

• Importance of CH$_3^*$ and C$_3$H$_3^*$ in soot formation

• Importance of other pathways involving dehydrogenation

• FTIR diagnostics in microchannels
• Line of sight absorbance measurements yield species concentration and temperature profile.
Absorption Theory

\[ \log_{10} \frac{I_0(\overline{\nu})}{I(\overline{\nu})} = A(\overline{\nu}) = \varepsilon(\overline{\nu}) C L \]

Absorbance

- Area under band head proportional to concentration.
- Shape of band head depends on \( T \)

\[ T = 575 \, K ; A_{\text{band}} = 980.49 \]

\[ T = 1400 \, K ; A_{\text{band}} = 990.41 \]
Measurement Method

• Temperature
  – Gas Temperature (FTIR)
    • Absorption spectrum of CO₂ measured from experiment
    • Fitting routine (EM2C, statistical narrow band model) employed to find best fit to experiment
    • Input temperature for the occurrence of best fit inferred to be the gas temperature.
  – Outer Wall Temp. distribution (IR Camera)
    • Wall temperature distribution inferred from infrared camera measurements (FLIR ThermaCam)
    • Calibrated using thermocouple

• Flame speed (mass-flow meters)
T Profile Along Line of Sight

- Must assume functional form of temperature profile.
  - Can’t solve for temperatures in each cell directly because the measurement responds to the product of the absorbance in each cells.
  - Guidance from analytical models
- Found that a 4\textsuperscript{th} order polynomial works reasonably well.

\[
T(y) = a_4 y^4 + b_4 y^3 + c_4 y^2 + d_4 y + e_4
\]
Pre and Post Flame T Profiles

- Transverse profiles have expected shapes
  - Pre-flame profiles indicate heat transfer from wall to gas
  - Post-flame indicate heat transfer from gas to wall
Heat recirculation map
Previous Work

• **C₃H₃** spectroscopy

• **CH₃** spectroscopy
Diagnostic Approaches

Infrared Diagnostics:
Diagnostic Approaches

Infrared Diagnostics:
Diagnostic Approaches

Inlet Press.

Probe beam

Choked Orifice

Traverse

Fuel Products

End View

Side View

YAG Laser

Dye Laser

ICCD

Spectrometer

Lock-in Amplifier

PMT

Freq. Doubler

Quartz windows

Collimated UV beam (332.5 or 216.6 nm)

Catalyst

Dye Laser

YAG Laser

Wave Meter

PMT

Lock-in Amplifier

I/I_0

Xe Spectrometer

Tub Furnace

CaF_2 windows

Water-cooled optical fibers

Catalyst

Pressure Vessel
(~350 psi)

End View

ICCD

Broadband Diagnostics:
**Apparatus**

- Tube Furnace (1100 K)
- Pressure Vessel
- N₂ Pressure Controller
- Independently Set System Pressure
- Independently Set Temperature
- Pump
- Independently Set Fuel Flow Rate
- Test Section
- Shell and Tube heat exchanger condenses reaction products for safe ejection
- Condensed Fuel
- Window
- Traverse
- Water
- Choked Orifice Flow Meter
- P, T
- N₂
Test Section

- Channel x-section: 4 mm x 4 mm
- Steel frame supports windows and spacers
- Apparatus supports little pressure difference because it is inside a pressure vessel
  - Can seal with ceramic wool
Test Section

- Spacer / Catalyst substrate
- Flow
- Steel Frame
- ZnSe, CaF$_2$, or Quartz Window
Experiment Design

• Channel Velocity Range:
  – Design Peclet number: $0.1 < Pe < 100$
    
    $$Pe = Re \times Sc = \frac{\rho uL}{\mu} \times \frac{\mu}{\rho D} = \frac{uL}{D}$$

  – Cantera used to compute $D$ of various species into $N_2$

<table>
<thead>
<tr>
<th>Solute (diffusion into $N_2$)</th>
<th>$D$ (m$^2$/sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (H$_2$)</td>
<td>1.39e-5</td>
</tr>
<tr>
<td>Methane (CH$_4$)</td>
<td>4.22e-6</td>
</tr>
<tr>
<td>Ethylene (C$_2$H$_4$)</td>
<td>3.20e-6</td>
</tr>
<tr>
<td>Benzene (C$_6$H$_6$)</td>
<td>1.82e-6</td>
</tr>
<tr>
<td>Dodecane (nC$<em>{12}$H$</em>{26}$)</td>
<td>1.11e-6</td>
</tr>
</tbody>
</table>

  – Density corresponds to $N_2$ at 1 to 50 atm.
  – Velocity range: $0.000121 < u < 0.12$ m/s
Experiment Design

• Mass flow
  – 100 % N$_2$ (infinite dilution)
    • Density of N$_2$ at 50 atm and 1100K is 15.4 kg/m$^3$.
    • Mass flow ranges from 2.99e-8 kg/sec (1.52 SCCM) to 2.99e-5 kg/sec (1520 SCCM).
  – 10% Dodecane, 90 % N$_2$ (minimum dilution)
    • Density of mixture at 50 atm and 1100K is 23.095 kg/m$^3$
    • Mass flow ranges from 4.47e-8 kg/sec (44.7 ug/sec) to 4.47e-5 kg/sec (44.7 mg/sec)
    • The minimum required volumetric flow rate of dodecane is 1.43 $\mu$l/min. This is approximately the lower range of the Eldex 1IMP metering pump (2 $\mu$l/min to 2.5 ml/min).

• Condenser
  – Maximum heat load is 62.3 J/s
  – $\Delta h_{\text{evap,H}_2\text{O}} = 2257$ J/g so should be easy to cool to 100°C by immersing coil in water bath and letting water boil on coil.
Experiment Design

- Minimum $Pe \sim 0.5$
- $Re$ range: $\sim 0.4 - 400$
Pressure Vessel/Heater Design

- Cost $D^2$ so custom heater better than COTS tube furnace
- 3 zones for better temperature uniformity
Anticipated Wall Temperature

- Core temperature ~1100 K (1520 F)
- Expect wall T to be ~ 250 F (<< 500 F limit)
Heater Tests

Thermocouple port
Window

Temperature controller
Heating elements
Pressure Vessel

- Manufacturer: Zeyon Inc., Bethlehem PA
- Inner dimensions: 9.0 in dia x 24 in long
- Material: 304 SS
- Weight: ~900 lb
- ASTM rating: 700 psi @ 500 F (47.6 atm, 533 K)
Pressure Vessel
Integration

Pressure Vessel

Window

FTIR

Optical Breadboards
Integration
FTIR Tests

Locations of molecules of interest on a background scan
FTIR Tests

The spectrum matches Polystyrene.
The best match value is 92.97 and the critical match value is 50.00.

Passed tests with NIST-traceable polystyrene samples
FTIR Tests

Multimode Fiber

External Detector
FTIR Tests

Multimode Fiber

Gas Cell
FTIR Tests

![FTIR Tests Graph](image)

- **NIST CH₄, 0.2 atm**
- **NIST CO₂, 0.26 atm**
- **NIST H₂O, liquid**
- **UMD CH₄, 1 atm**

**Wavenumber (cm⁻¹)** vs. **Transmittance (I/I₀)**

The graph shows the transmittance of different gases at various wavenumbers.
Status / Next Steps

• Main components of experiment are ready
• Awaiting arrival of pressure vessel
  – Install ceramic liner, heaters, test section, pressure control, thermocouples, etc.
• Leak/safety tests at temperature and pressure
• Preliminary absorption measurements in vessel
  – Species: 100% N₂; 2% CH₄ and C₂H₂ (in N₂)
  – Pressures: 1, 10, 20, 40 atm
  – Temperatures: 300, 500, 1000 K
  – Static conditions followed by flowing conditions
  – Objectives:
    • Acquire baseline absorption spectra
    • Gauge importance of pressure broadening
Homogeneous Endothermic Reaction

\[ q_{\text{Engine}} = q_{\text{Fuel}} \]

\[ q_{\text{Engine}} = q_{\text{Fuel}} = \dot{m}_f \Delta H_{\text{fluid}} \]
Heterogeneous Endothermic Reaction

\[ q_{\text{Engine}} \neq q_{\text{Fuel}} \]

\[ q_{\text{Engine}} + q_{\text{Fuel}} = m_f \Delta H_{\text{surf}} \]
Fuel Bourne Catalyst

\[ q_{\text{Engine}} = q_{\text{Fuel}} \]
## Injection Conditions

<table>
<thead>
<tr>
<th></th>
<th>Gas Turbine&lt;sup&gt;1-3&lt;/sup&gt;</th>
<th>Scramjet&lt;sup&gt;1,4&lt;/sup&gt;</th>
<th>Rocket&lt;sup&gt;5-9&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection pressure drop ($\Delta P$), psi</td>
<td>50-200</td>
<td>&lt; 500</td>
<td>250-4000 (jacket + injector $\Delta p$)</td>
</tr>
<tr>
<td>Chamber pressure, psi</td>
<td>&lt; 620</td>
<td>-</td>
<td>125-3000</td>
</tr>
<tr>
<td>Injection pressure, psi</td>
<td>&lt; 820</td>
<td>-</td>
<td>325-7000</td>
</tr>
<tr>
<td>Chamber Temperature, K</td>
<td>&lt; 1873</td>
<td>-</td>
<td>3600 (LOX, H&lt;sub&gt;2&lt;/sub&gt;)</td>
</tr>
</tbody>
</table>

References:

Major Interferences in Dodecane Cracking (25 atm, 1100K)

\[ \text{Transmissivity (\%)} \]

- \( \text{CH}_4 \)
- \( \text{C}_2\text{H}_2 \)
- \( \text{C}_2\text{H}_4 \)
- \( \text{C}_2\text{H}_6 \)
- \( \text{CH}_3^* \)
- \( \text{C}_2\text{H}_3^* \)
- \( \text{C}_3\text{H}_3^* \)
- \( \text{C}_6\text{H}_5^* \)

\[ \text{cm}^{-1} \]
Limitations/Solutions

- Interference from CO and Silicon
  - Fitting only between 2250-2300 cm\(^{-1}\)
- Loss of transmissivity with increase in T (> 350 °C)
  - Stoichiometric eq. ratio not explored

\[X_{CO} = 0.04, \quad X_{CO_2} = 0.076, \quad X_{H_2O} = 0.2, \quad X_{CO} + X_{CO_2} + X_{H_2O}\]

\[\phi = 1, \quad U = 60 \text{ cm/s}\]