High-Pressure Turbulent Flame Speeds and Chemical Kinetics of Syngas Blends With and Without Impurities

Eric L. Petersen
Department of Mechanical Engineering
Texas A&M University

2015 University Turbine Systems Research Workshop
Atlanta, GA
3-5 November, 2015
Project Overview

3-Year Project Began in October, 2013

Project Highlights:


2. DOE NETL Award DE-FE0011778

3. Budget: $498,382 DOE + $124,595 Cost Share

4. Principal Investigator: Dr. Eric L. Petersen
Project Overview

This Project Addresses Several Problems for HHC Fuels

1. Improve **NOx kinetics** for High-Hydrogen Fuels at Engine Conditions

2. Effect of **Contaminant Species** on Ignition and Flame Speed

3. Impact of **Diluents** on Ignition Kinetics and Flame Speeds

4. Data on **Turbulent Flame Speeds** at Engine Pressures
There are Five Main Work Tasks for the Project

Work Tasks:

**Task 1** – Project Management and Program Planning

**Task 2** – Turbulent Flame Speed Measurements at Atmospheric Pressure

**Task 3** – Experiments and Kinetics of Syngas Blends with Impurities

**Task 4** – Design and Construction of a High-Pressure Turbulent Flame Speed Facility

**Task 5** – High-Pressure Turbulent Flame Speed Measurements
Project Overview

**TAMU** Work is a Team Effort of Several People

Dr. Olivier Mathieu

Charles Keesee

Anibal Morones

Clayton Mulvihill
Task 2 – Turbulent Flame Speed Measurements at Atmospheric Pressure
1-atm Turbulent Flame Speed Measurement will Build Upon Tests Done in Previous UTSR Project

- Utilize Existing Turbulent Flame Speed Hardware
- Extend Test Conditions to a Range of $u'$ and Length Scale Values
- Detailed Characterization of Existing Conditions with LDV
- Perform Experiments for Syngas Blends at 1 atm Conditions
Task 2 – Turbulent Speeds

Existing 1-atm Rig Characterized for 1 Main Condition

Features:

• 7075-T6 Heat-Treated Aluminum
• 4 radial impellers
• Diameter: 30.5 cm
• Length: 35.6 cm
• Window Port Diameter: 12.7 cm
• Maximum initial pressure: 1 atm
• Maximum initial temperature: 298 K

Turbulence:

• Intensity: \(1.5 \text{ m/s rms}\)
• Integral length scale: 27 mm
Task 2 – Turbulent Speeds

Existing Rig Has 4 Fans Centrally Located, Added to Original Rig of de Vries (2009)
## Task 2 – Turbulent Speeds

### LDV Setup from TSI

<table>
<thead>
<tr>
<th>Device</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transceiver</td>
<td>PowerSight TR-SS-2D</td>
</tr>
<tr>
<td>Signal processor</td>
<td>FSA4000-2</td>
</tr>
<tr>
<td>Traverse</td>
<td>Isel T3DH</td>
</tr>
<tr>
<td>Photomultiplier</td>
<td>PDM1000-2SS</td>
</tr>
<tr>
<td>Particle Generator</td>
<td>9306</td>
</tr>
<tr>
<td>Computer</td>
<td>Dell Precision T7600</td>
</tr>
</tbody>
</table>
Task 2 – Turbulent Speeds

Optics Alignment
Task 2 – Turbulent Speeds

*Collocating the probe volume and the receiving optics*
Task 2 – Turbulent Speeds

Timing Sequence Controlled to Capture Turbulence

Test region
$6 \times 6 \times 6 \text{ cm}^3$
Task 2 – Turbulent Speeds

Turbulent Fluctuation rms Results

\[ u_{i,rms}(x) = u_i^{2/2}(x) = \sqrt{\frac{1}{N} \sum_{n=1}^{N} (u_i(t_n;x))^2} \]

Test region average: horizontal 1.60 m/s; vertical 1.63 m/s
## USC simulations

### Agreement with numerical model

<table>
<thead>
<tr>
<th>Reference</th>
<th>Technique</th>
<th>Turbulence fluctuation</th>
<th>Average velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ravi, Peltier et al. 2013)</td>
<td>PIV</td>
<td>1.48</td>
<td>0.03</td>
</tr>
<tr>
<td>(Davani and Ronney 2015)</td>
<td>Simulation</td>
<td>1.63</td>
<td>0.12</td>
</tr>
<tr>
<td>This work</td>
<td>LDV</td>
<td>1.62</td>
<td>0.40*</td>
</tr>
</tbody>
</table>

*axial
Task 2 – Turbulent Speeds

Turbulence Homogeneity and Isotropy

\[
H_i(x) = \frac{u_{i,rms}(x)}{u_{i,rms}}
\]

\[
I_{xy}(x) = \frac{u_{x,rms}(x)}{u_{y,rms}(x)}
\]

Horizontal turbulence fluctuation homogeneity
XY Cross section at Z = 0mm

Turbulence fluctuation isotropy
XY Cross section at Z = 0mm

\[
u_{i,rms} = \frac{1}{M} \sum_{1}^{M} u_{i,rms}(x_m)
\]

Isotropy test region average 0.98
## Task 2 – Turbulent Speeds

Integral time scale comparable to flame experiment duration

<table>
<thead>
<tr>
<th>Run #</th>
<th>Location</th>
<th>Integral time scale [ms]</th>
<th>Taylor microscale [ms]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Horizontal</td>
<td>Vertical</td>
</tr>
<tr>
<td>285</td>
<td>0, 0, 0</td>
<td>13.5</td>
<td>12.5</td>
</tr>
<tr>
<td>1112</td>
<td>30, 0, 0</td>
<td>10.2</td>
<td>8.5</td>
</tr>
<tr>
<td>943</td>
<td>-30, 0, 0</td>
<td>10.5</td>
<td>8.8</td>
</tr>
<tr>
<td>1015</td>
<td>0, 30, 0</td>
<td>11.3</td>
<td>11.6</td>
</tr>
<tr>
<td>1040</td>
<td>0, -30, 0</td>
<td>13.2</td>
<td>15.9</td>
</tr>
<tr>
<td>436</td>
<td>0, 0, 30</td>
<td>12.4</td>
<td>11.4</td>
</tr>
<tr>
<td>1592</td>
<td>0, 0, -30</td>
<td>10.1</td>
<td>9.9</td>
</tr>
</tbody>
</table>

\[
\Lambda_t \equiv \int_0^\infty r(\tau) d\tau \quad \lambda_t^2 \equiv -2 \left. \frac{\partial^2 r}{\partial \tau^2} \right|_{\tau=0}
\]
Task 2 – Turbulent Speeds

Results Indicate a (Slow) Overall Vortex Pattern
Task 2 – Turbulent Speeds

2-D Average Velocity Results

- Radial pattern
- Test region average 0.58 m/s
1. Results agree qualitatively with the previous work of Ravi (2013).

2. HIT turbulence confirmed

3. Extension of measurements to a 3-D region revealed unfavorable characteristics previously missed.

4. The axial component found to have a resultant mean flow of 0.4 m/s.

5. A regular polyhedron fan distribution is advised
Task 3 – Experiments and Kinetics of Syngas Blends with Impurities
Task 3 – Impurity Effects

Overall Task Has 2 Main Goals

1. Study Impurity Composition Effect
   • Ignition delay time ($\tau_{\text{ign}}$) measurements in a shock tube
   • Laminar flame speed measurements
   • Large range of P, T

2. Kinetics Modeling of Impurities
Update Today Will Focus on 2 Main Projects

1. **H₂S Impurity** Effect on Laminar Flame Speeds for Coal Syngas

2. **H₂S Oxidation Kinetics** and Shock-Tube Measurements
Task 3 – Impurity Effects

High-Temperature, High-Pressure Vessel Used for Laminar Flame Experiments

Vessel Internal Dimensions:

31.8 cm Diameter
28 cm Length
12.7 cm Window Diameter
Task 3 – Impurity Effects

*Laminar Flame Speed* Measurements Performed With $H_2S$ Impurity

- Baseline “coal” syngas: 60% CO / 40% $H_2$
- Equivalence ratio Sweep
- Pressure: 1 atm
- $H_2S$: 1% by Volume
- **Argon** instead of $N_2$
### Task 3 – Impurity Effects

**Mixtures Investigated for Flame Speed Study**

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Fuel</th>
<th>Oxidizer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
<td>H₂</td>
</tr>
<tr>
<td>Coal - Neat, Air</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Coal - Neat, Argon</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Coal - 1% H₂S, Argon</td>
<td>0.594</td>
<td>0.396</td>
</tr>
</tbody>
</table>

O₂/Ar ratio chosen to match Flame Temp with air over same φ range
Task 3 – Impurity Effects

$H_2S$ Has Small Effect and Only for Rich Mixtures

Model: NUIG mechanism with TAMU $H_2S$ kinetics
Argon-Based Flame Speeds Noticeably Lower than $N_2$-Based Ones
Argon-Diluted Mixture Markstein Lengths

$L_b (cm)$

Coal, Ar - Neat, Markstein
Coal, Ar 1% H2S, Markstein

$\phi$
Task 3 – Impurity Effects

Air and Argon/O$_2$-Based Markstein Lengths are Similar
Shock-Tube Experiments Focused on $H_2S$ Oxidation

Task 3 – Impurity Effects

- $H_2S$ – $O_2$ – Argon mixtures (98% Ar dilution)
- Equivalence ratios: 0.5, 1.0, 1.5
- Pressure: 1.7 atm
- Ignition delay times
- Water concentration time histories
Task 3 – Impurity Effects

High pressure shock-tube facility at Texas A&M

High-Pressure Shock-Tube Facility

- 1 – 100 atm Capability
- 600 – 4000 K Test Temperature
- Up to 20 ms Test Time
- 2.46 m Driver and 4.72 m Driven
- 15.24 cm Driven Inner Diameter

Vacuum System

Driven Section (4.72 m)  Driver Section (2.46 m)

Expansion Section / Diaphragm Location

Access Port

Weldless Flange

Time-Interval Measurement
Task 3 – Impurity Effects

Ignition Delay Time Obtained from OH* Time History

- $A^2 \Sigma^+ (OH^*)$ light at 307 nm
- Highly Diluted Mixtures (98% Ar)
Task 3 – Impurity Effects

_Tunable laser diagnostic used for transient H₂O concentrations_

- Control and monitoring of laser
  - Toptica Photonics DL 100: CW, narrow width laser
  - Toptica Photonics DC 110: current and temperature control
  - Burleigh WA-1000: monitoring of laser wavelength

- Common mode rejection

- Lexan enclosures
  - Purged by N₂
  - Monitored by hygrometer
  - < 0.1% RH for all experiments
The temperature rise due to combustion causes a significant change in the absorption coefficient

- Temperature rise simulated by CHEMKIN (typically 200-300 K)
- In-house routine created to correct raw data with simulated temperature rise
- Modified mechanisms used to iterate on accurate solution

Absorption coefficient vs. time and simulated temperature:

- Absorption coefficient (cm\(^{-1}\) atm\(^{-1}\))
- Simulated temperature (K)

Time (milliseconds) vs. Absorption coefficient (cm\(^{-1}\) atm\(^{-1}\)) for 1560 K, 1.31 atm, 0.008 H\(_2\)S / 0.012 O\(_2\) / 0.98 Ar.
Typical OH* and H$_2$S Time Histories Show Main Ignition During Middle of Water Formation

H$_2$S in 98% Ar, $\phi=1.0$

- H$_2$O (1611 K, 1.29 atm)
- OH* (1620 K, 1.07 atm)
First Ignition Delay Time Results Obtained for $H_2S$ Oxidation

Task 3 – Impurity Effects
Task 3 – Impurity Effects

Kinetics Modeling of Ignition is Ongoing…

- All recent literature based on model from Zhou, Haynes, et al., 2013
- Original model from Zhou et al. not in good agreement with the new set of data.
- Model from Mathieu, Petersen et al. (2014) not working well here.
- This study: fair agreement with new data and w/ former literature ST data => new meas. helpful
- Not possible to reconcile both shock tube and flow reactor data w/ current models.
Task 3 – Impurity Effects

Kinetics Model Predicts Shape of $OH^*$ Time History Rather Well

This study
Task 3 – Impurity Effects

Water Time Histories Provide Valuable Information for Improving H₂S Kinetics Mechanism

Effect of Temperature

- H₂S in 98% Ar, φ = 1.0
- 1515 K, 1.35 atm
- 1685 K, 1.29 atm
- 1784 K, 1.25 atm

Effect of φ

- H₂S in 98% Ar
- 1774 K, φ = 0.5
- 1784 K, φ = 1.0
- 1776 K, φ = 1.5
Task 3 – Impurity Effects

H$_2$O Profiles Uncovered Large Deficiencies in Previous Mechanisms…

- All recent models predict H$_2$O starting too early
- Mainly due to $\text{H}_2\text{S} + \text{O}_2 = \text{SH} + \text{HO}_2$ (R1)
- R1 rate needs to be modified
- Rate of SH + O$_2$ = HSO + O changed w/rate meas. in lit.
- Other rxns. suspicious ($\text{SH} + \text{SH} + \text{M} = \text{HSSH} + \text{M}$)
- More data at different conditions and rate measurements sorely needed!
Task 4 – Design and Construction of a Turbulent Flame Speed Facility
Task 4 – New Facility

Borghi Diagram shows Current and Desired Regions for Turbulent Flame Speeds
New Facility Will be Designed and Built at TAMU

1. Detailed Design and Structural Analysis

2. Fabrication of Vessel Components

3. Installation of Vessel

4. Characterization of Flow Conditions
Task 4 Design and Installation is Underway

- Survey of Existing Turbulent Flame Speed Facilities Completed

- Trade-off Study for Final Design Finished

- Critical Aspect is how to Handle or Reduce the Overpressure

- Will Move Toward a Design that Involves a Blowout Disk and Reservoir for Overpressure

- Detail Design is Complete

- Fabrication is Underway
New Design is Complete

- Built in forged SS
- ID 14”; height 18”
- 4 windows; Ø5” aperture
- 4 stirring fans; Ø5.75”
- Max. allowable pressure: 200 atm
Task 4 – New Facility

*Breach and Diaphragm Method Selected for Venting*

- Breach Ø8"
- Vented deflagration through diaphragm (top)
- Bottom breach is reconfigurable:
  - Heater
  - Injection port
  - Spark plug gland
Task 4 – New Facility

New Fan Design was Implemented, Based on LDV Results from Existing Rig

- Arranged in tetrahedral configuration
- Max. speed: 10,000 rpm
- 8-bladed radial impeller with 30° pitch and 1.25” axial depth.
• Fused quartz substrate

• Two orthogonal lines of sight

• Size and proportions of window and vessel have been proven to produce data free of ignition and confinement effects.
Task 5 – High-Pressure Turbulent Flame Speed Measurements
High-Pressure Experiments Will be Performed for Selected Syngas Blends

- Identify Two Test Matrices (Fuel Blends) for Study
- Utilize Results from Tasks 2 and 3 for Guidance
- Perform Experiments at Elevated Pressures
- Parallel High-Pressure Laminar Tests Should also be Done
Progress on the Five Main Work Tasks for the Project Was Presented

Task 1 – Project Management and Program Planning

Task 2 – Turbulent Flame Speed Measurements at Atmospheric Pressure

Task 3 – Experiments and Kinetics of Syngas Blends with Impurities

Task 4 – Design and Construction of a High-Pressure Turbulent Flame Speed Facility

Task 5 – High-Pressure Turbulent Flame Speed Measurements
Task 2 – Turbulent Speeds

Recent Data Cover a Wide Range of Flamelet Regions

- CH₄
- Syngas
- 50-50 CH₄-H₂
- H₂

Distributed Reactions

Thin Reaction Zone

Ka = 1

Reₜ = 1

L/δ

Da = 1

Lamellar Flame

Wrinkled Flamelet

Corrugated Flamelet

Thin Reaction Zone

Distributed Reactions

Recent Data Cover a Wide Range of Flamelet Regions