Flame Studies of Small Hydrocarbons and Oxygenated Fuels

Peter Veloo, Yang Lee Wang, Qiayo Feng, Fokion N. Egolfopoulos

Department of Aerospace and Mechanical Engineering
University of Southern California

MULTI AGENCY COORDINATION COMMITTEE FOR COMBUSTION RESEARCH (MACCCR)
FUELS RESEARCH REVIEW

September 20-23, 2010
Princeton, New Jersey

Combustion Energy Frontier Research Center (CEFRC)
DoE Grant: DE-SC0001198
Period of performance: 8/1/09 – 7/31/14
Technical Monitor: Dr. Wade Sisk
General Objectives and Some “Top-View” Issues

1. To determine archival fundamental flame data for oxygenate fuels that are of relevance to transportation:
   • flame propagation $\sim (\text{rxn rate})^{1/2}$
   • flame ignition
   • flame extinction
   • $\text{NO}_x$ concentration structures
   • soot volume fraction profiles

1. To model experiments using detailed description of chemical kinetics and molecular transport. **Issues:**
   • **CFD:** experimental boundary conditions MUST be used
   • **kinetic models for oxygenated fuels:**
     » (A) model DOES NOT exist
     » (B) model DOES exist:
     • notable differences in fuel kinetics
     • notable differences in $\text{C}_0$-$\text{C}_4$ kinetics

1. To provide insight into the effects of the location and type of the O-containing functional group as a function of the carbon number on the fuel oxidation in flame environments.
Parameter Space

- **Fuels:**
  - DME (target)
  - C\(_1\)-C\(_4\) alcohols (target)
  - C\(_1\)-C\(_{10}\) methyl & ethyl (saturated & unsaturated) esters (target)
  - **aldehydes (supporting)**
  - **ketones (supporting)**
  - H\(_2\) and CO (supporting)
  - C\(_1\)-C\(_4\) \(n\)-alkanes and \(n\)-alkenes (supporting)

- **Reacting configurations:**
  - premixed
  - non-premixed

- **Thermodynamic conditions:**
  - wide range of reactant and inert compositions
  - initial reactant temperatures:
    - ambient to 500 K
  - pressures:
    - 0.5 to \(~15\) atm (present capabilities)
    - 20-50 atm (projected)
Experimental Approach

- Use of counterflow technique to measure laminar flame speeds and ignition/ extinction limits

- Pressure chamber:
  - Pressure range 0.1-15 atm

- Diagnostics:
  - Digital Particle Image Velocimetry (DPIV)
  - Thermocouples
  - Intrusive NO$_x$ sampling
  - Laser extinction
Numerical Approach

- Use of CHEMKIN-based codes

- Proper description of “turning-point” behavior

- Mathematically rigorous determination of logarithmic sensitivity coefficients: \( \frac{\partial (\ln Y)}{\partial (\ln X)} \)
  - \( Y \): laminar flame speed / extinction strain rate / ignition temperature
  - \( X \): A-factor / \( D_{i-N_2} \)

- All numerical results have been produced by solutions that:
  - Were properly converged, i.e. in highly resolved grids
  - Included the effects of thermal radiation and Soret
  - Included full multi-component transport formulation
  - Included all pertinent experimental boundary conditions
1. Flame studies of neat and mixtures of H₂/CO/C₁₄ hydrocarbons  
   » (33rd Combustion Symposium, 2010)

1. Flammability limits of CH₄/air mixtures at elevated pressures  
   » (33rd Combustion Symposium, 2010)

1. Flame studies of butanol isomers  
   » (33rd Combustion Symposium, 2010)

2. Extinction of DME and ethanol flames  
   » (33rd Combustion Symposium, 2010)

3. NOₓ formation in methyl-ester flames  
   » (Industrial and Engineering Chemistry Research, 2010)

4. Studies of methanol, ethanol, and n-butanol flames  
   » (Combustion and Flame, 2010)

5. Studies of n-propanol, iso-propanol, and propane flames  
   » (Combustion and Flame, 2010)

6. Studies of C₄ and C₁₀ methyl-ester flames  
   » (Combustion and Flame, 2010)
Oxidation of methanol represents an extreme case – formaldehyde (CH₂O) produced directly from fuel consumption reactions.

Branching reduces reactivity through the production of resonantly stable intermediates.

Modeling of propagation of n-butanol flames


Laminar flame speed, \( S^0_u \), cm/s

Equivalence Ratio, \( \phi \)

\[ p = 1 \text{ atm} \]
\[ T_u = 343 \text{ K} \]
Effect of $\text{H}_2/\text{CO}$ and $C_1$-$C_4$ hydrocarbon kinetics

- Model P2 superimposes the propanol chemistry by Curran and coworkers onto the USC Mech II $\text{H}_2/\text{CO}$ and $C_1$-$C_4$ for analytical purposes.

Ignition of non-premixed C₃ and C₄ alcohol flames

- Trends previously noted are repeated in ignition data to a large extent.
- Branching again leads to lower reactivity, i.e. larger ignition temperature.

$p = 1 \text{ atm}$  
$T_u = 473 \text{ K}$  
$K_{\text{global}} = 135 \text{ s}^{-1}$
**Major intermediates in C₃ and C₄ alcohol flames**

### C₃ Alcohols – Major intermediates (e.g.)

- C–C–C–OH
- C–C–C
- Propionaldehyde
- Acetone
- Propene

### C₄ Alcohols – Major intermediates (e.g.)

- C–C–C–C–OH
- C–C–C–C–C
- Butyraldehyde
- Butanone
- iso-Butyraldehyde
- 1-Butene
- 2-Butene
- iso-Butene
Preliminary flame propagation results: aldehydes and ketones

- Preliminary results indicate that the aldehydes are more reactive than their equivalent ketones

**C₄ & C₁₀ methyl esters – Experimental flame propagation data vs. recent models**

**Methyl butanoate**

![Graph showing laminar flame speed (Sₜ) vs. equivalence ratio (Φ) for methyl butanoate with data points and models MB1, MB2, MB3, and MB4.](image)

- **Tᵢ = 403 K**

**Methyl decanoate**

![Graph showing laminar flame speed (Sₜ) vs. equivalence ratio (Φ) for methyl decanoate with data points and models MD1.](image)

- **Tᵢ = 403 K**


• Presence of the methyl ester group lowers overall reactivity, especially on the lean side. Effect diminishes as carbon chain length increases.

• Double bond in unsaturated methyl ester increases overall reactivity, with the effect mainly being through higher temperatures.

**C4 & C10 methyl esters – Experimental flame extinction data vs. recent models**


**Effect of Lennard-Jones potential parameters**

Methyl butanoate – N₂


- Using newly estimated values of $D_{MB-N₂}$ resulted in >50% reduction in the computed $K_{ext}$’s, underlining the importance of using consistent and accurate sets of L-J parameters in the transport databases.

---

**Preliminary Results: Smaller methyl & ethyl esters**

- Ethyl ester flames propagate faster than their methyl counterparts
- Methyl or ethyl acetates propagate slower than formate and propanoates flames
Comparisons of soot volume fractions

$p = 1$ atm
$T_u = 403$ K
$K_{\text{global}} = 30$ s$^{-1}$
NO$_x$ measurements for n-butane/air and methyl butanoate/air flames

$\phi = 0.8$, $T_u = 333$ K, $K_{global} = 168$ s$^{-1}$

$n$-butane/air $>$ methyl butanoate/air

Same flame temperature:

$n$-butane/air $\sim$ methyl butanoate/air

$\phi = 1.2$, $T_u = 333$ K, $K_{global} = 168$ s$^{-1}$

$n$-butane/air $>$ methyl butanoate/air

Same flame temperature:

$n$-butane/air $>$ methyl butanoate/air
1. Fundamental flame properties were investigated experimentally and computationally at atmospheric pressure for C$_1$-C$_{10}$ oxygenated fuels:
   - ethers
   - alcohols
   - methyl and ethyl esters
   - ketones
   - aldehydes

2. The effects of O-containing functional group, carbon number, branching, and extent of saturation were assessed on:
   - flame ignition, propagation, and extinction
   - NO$_x$ formation propensity
   - soot formation propensity

3. Notable deficiencies were identified in various existing models attributed to:
   - fuel-related kinetics
   - (foundation) C$_0$-C$_4$ kinetics
   - fuel transport properties

4. Conventional and unconventional approaches are considered to perform *direct measurements* and probe flame kinetics at high pressures (20 - 50 atm range)