

Background

- Recent studies of the effect of oxygenated fuels on particulate formation under Diesel engine combustion conditions show that
 - particulate emissions are significantly reduced
 - the emissions reductions depend on both the amount of oxygen in the fuel and the oxygenate structure
- Using oxygenated fuels to replace or supplement petroleum-based fuels in high-efficiency Diesel engines is a promising technology for reducing greenhouse gas emissions from the transportation sector.
- A systematic study of oxygenated fuel combustion is needed to optimize fuel structure with respect to emissions and best performance.
- Several oxygenated fuels with potential for particulate emissions reduction from Diesel engines have been identified, including dimethyl ether, acetone and butanol.
- Here, we present initial results from a flow reactor experimental investigation of dimethyl ether (DME) oxidation.

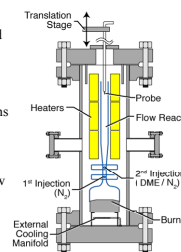
Objectives

- Acquire experimental data to use in refinement, optimization and reduction of detailed reaction mechanisms for oxygenated fuels.
- Assess model fidelity through complementary flow reactor and shock tube experiments.
- Study a set of representative oxygenated fuels with different oxygen functionality (ethers, ketones, esters, aldehydes) in order to access a variety of soot formation pathways.

*Robert D. Cook, David F. Davidson, Ronald K. Hanson, *Oxidation Chemistry of Selected Oxygenate Fuels: Dimethyl Ether, Acetone, and Butanol*

Experimental Facility

- Quartz flow reactor
- Combustion-driven (premixed H₂/Air, $\Phi \sim 0.95$)
- Pressures 1-20 bar
- Temperatures < 1400K
- Total residence times 20-100 ms
- Fuel and cooling nitrogen are injected through radially opposed injectors oriented perpendicular to the main flow
- 2-stage injection provides excellent mixing
- Electrical resistance heaters provide nearly adiabatic conditions



Experimental Facility (cont.)

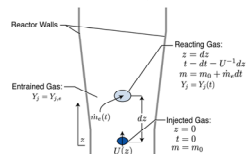
- Thermocouple and extractive sampling along reactor centerline
 - R-type thermocouple with 100 mm bead diameter and 25 mm SiO₂ coating
 - +/- 5 K accuracy
- Gas sampling
 - Extracted and quenched in a cooled probe for online analysis
 - Heated sample transfer for condensable species
 - Diagnostics
 - μ -GC/TCD (HC's, CH₂O, H₂, H₂O)
 - NDIR (CO, CO₂)
 - Paramagnetic (O₂)

Approach

- The centerline gas temperature and stable species concentrations are measured at ambient pressure and elevated temperature.
- Velocity measurements are used to infer the residence time at each measurement location.
- The effect of pressure, temperature and reactant concentration on reaction timescales, heat release rate and intermediate and product species profiles are determined for rich conditions.
- The measured species and temperature profiles are compared to the model predictions using a detailed reaction mechanism.

Reacting Flow Model

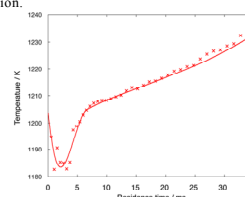
- Mixing-reacting model is based on reactor flow conditions and measured temperature profiles, with boundary-layer correction from centerline velocity measurements.



- DME mechanism "LLNL": H. J. Curran, *Unpublished Proceedings of the European Combustion Meeting, 2003* (available from http://www-cms.llnl.gov/combustion/combustion_home.html)
- 582 species, 2603 reactions

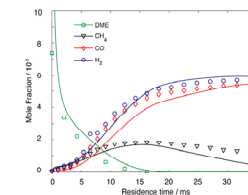
Results

- Rich DME experiments ($\Phi = 2$) have been conducted at 1 atm with an initial temperature of 1200 K.
- The reactor flow rates, geometry and measured temperature profile are used as input to the mixing-reacting model simulation.



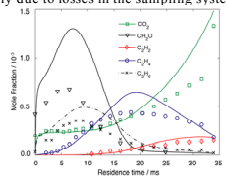
Major Species

- The mixing-reacting model provides very good agreement with measured major species profiles, especially for H₂ and CH₄.
- CO levels exceed the model prediction at intermediate times.

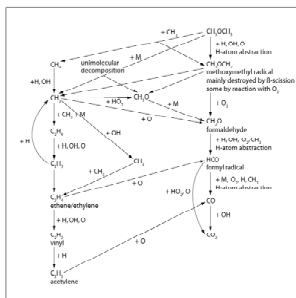


Minor Species

- Important soot precursors ethylene (~500 ppm) and acetylene (~100 ppm) are present. Formaldehyde levels up to 680 ppm are observed.
- Peak ethane and ethylene levels are below predicted values, while acetylene shows extremely good agreement with the model.
- Formaldehyde (CH₂O) measurements are lower than predicted, most likely due to losses in the sampling system.



Reaction Pathways



- DME is removed through unimolecular decomposition and radical attack.
- C₂-species ethylene and acetylene are precursors to aromatic production. The aromatics combine into polyaromatic hydrocarbons (PAHs) and ultimately become soot.

Conclusions

- The measured and predicted time-evolution of species concentrations are in relatively good agreement.
- At longer reaction times, measured carbon balance closes to better than 1%. At early times, only approximately 85% of the carbon can be accounted for due to loss of water-soluble species in the sampling system.
- Opportunities remain for improved accuracy in the measurement of water-soluble species like DME and formaldehyde. At present, the sampling system has been modified to improve these measurements.

Future work

- High pressure DME experiments
 - Experiments at pressures relevant to diesel combustion to investigate the effect of pressure on DME chemistry
- Comparison of DME experimental data with additional DME kinetic mechanisms available in the literature.
- Experiments with DME as an additive to heptane, a common component of diesel surrogates.
- Flow reactor experiments at conditions overlapping with shock tube experiments with representative oxygenates from other functional groups:
 - Acetone (a ketone)
 - Butanal (an aldehyde)
 - Dimethoxymethane (an ether)