Effects of Pressure on Hydrocarbon Oxidation Under Flameless Conditions

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Background
- Hydrocarbon combustion under the conditions of flameless oxidation—characterized by well-mixed, dilute, preheated reactants—is a promising technology that can improve thermal efficiency and reduce pollutant and greenhouse emissions.
- Though typically used in industrial furnaces, this process has the potential to deliver improved performance in work-producing devices by matching the time scales for chemical reaction and mechanical expansion.

Experimental Facility
- Flow Reactor
  - Pressure: 1-52 bar
  - Temperature: up to 1850°C
  - Excellent mixing due to two-stage hydrodynamics
  - Insulation and heaters provide nearly adiabatic conditions
  - Residence times up to 150 ms
- Thermocouple probe
  - 1-6 mm i.d. (O2/NO2, NO)
  - 100 mm bending diameter
  - 25 mm SO2 cooling
  - ± 1% accuracy
- Gas Sampling
  - Extracted and quenched in a water-cooled probe for online analysis
  - Heated sample transfer for corrosive species

Kinetic Model
- O-D transient reactor model (Chemkin 4.0)
  - Initial conditions set to measured species concentrations at the first well-mixed station
  - Simulation uses measured temperature profiles
  - 2000 elementary reactions among 129 species
  - Rate parameter temperature and pressure dependence for multi-channel reactions
  - Better agreement with experimental data than GRI-Mech 3.0, a standard hydrocarbon combustion mechanism

Results
- Experiments have been conducted at 1, 2 and 4 bar with initial temperatures of 1060–1160 K
- Measured heat-release rate differs slightly from the adiabatic prediction, although the time-scales are comparable
- Agreement between measured and predicted species concentrations is improved when the simulation is constrained to the measured temperature profile

Minor Species
- Moderate levels of H2, CH2O and CH4 with trace concentrations of C2H4 are observed
- The model tends to slightly over-predict the rates of CH4 production and CH2O removal, especially at higher pressures

Conclusion
- The measured and predicted time-evolution of temperature and species concentration are in relatively good agreement
- The current reaction mechanism accurately predicts the change in reaction time scales due to variations in pressure, temperature and composition
- More than 95% of the carbon present in the unburned fuel can be traced through intermediate species to products
- The presence of NO results in a small enhancement of oxidation rates at early times by contributing to the radical pool
- Opportunities remain for improved accuracy in the measurement and prediction of minor species concentrations

Approach
- Time-evolution of gas temperature and stable species concentration are measured along a nearly adiabatic combustion-driven flow reactor at ambient to elevated pressures and intermediate temperatures.
- Centerline 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.
- The measured species and temperature profiles are compared to the model predictions using a detailed reaction mechanism.

Objectives
- Assess model fidelity and validate experimental techniques
- Acquire experimental data to use in refinement, optimization and reduction of detailed reaction schemes
- Provide high quality experimental data for the development of improved hydrocarbon oxidation mechanisms
- Determine the influence of species from recirculated exhaust gas (e.g., H2O, CO2) and from trace concentrations of byproduct species (e.g., NO) on fuel oxidation rates
- Explore the impact of multi-channel reaction pathways on fuel oxidation

Major Species
- Measured carbon balance close to better than 5%
- Characteristic reaction time-scales increase with pressure

Reaction Pathway
- Hydroxyl radicals, generated primarily from reactions involving stable hydroperoxy radical, govern the oxidation of fuel and intermediates
- Radical attack, beta-scission and concerted elimination convert ethane to vinyl radicals
- Vinyl reacts with O3 to produce CH2=CH2O, which are subsequently converted to CO and CO2

Future work
- Broader range of experimental conditions
- Higher pressure, lower temperature to further explore the influence of alkylperoxy chemistry
- Optimization and reduction of the current mechanism
- Larger parent fuel (propane, butane)
- Negative Temperature Coefficient (NTC) behavior
- Oxygenated fuels