

Flow Reactor Study of Controlled Combustion Kinetics

Investigators

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Introduction

In conventional energy conversion devices (e.g., gas turbines and piston engines) useful work is produced in a two-step process: conversion of chemical energy to sensible energy by combustion, followed by work extraction by expansion. The first of the two processes typically occurs on a very short time scale and is essentially complete before the second process begins. The reaction between fuel and oxygen in these devices, yielding product species (H_2O , CO_2) and heat, is unrestrained and highly irreversible, resulting in a second law efficiency that is significantly less than unity. If this irreversibility can be reduced (i.e., modifying the process such that it is more reversible) then the efficiency of energy conversion is improved, resulting in fuel savings and decreased emission of CO_2 . One approach to accomplish this is by closely matching the rates of heat release and expansion, effectively extracting work while the reaction proceeds. The simultaneous reaction and work extraction is much like the fuel cell process. Matching heat release and expansion rates requires control of the combustion process.

Controlled combustion may be achieved by carefully controlling the temperature and composition of the reactants, thereby tailoring the rate at which fuel and oxygen react. This type of combustion, where the reaction rate is dominated by elementary reaction steps as opposed to heat or mass transport, may be achieved by a combination of waste heat recovery and exhaust gas recirculation¹. In addition to the improved thermal efficiency, this process decreases the peak flame temperature which can decrease NO_x emissions by orders of magnitude². The reduction in peak temperature may also help reduce heat losses in combustion devices, further improving efficiency. While various forms of controlled combustion have been investigated, commercial application has been limited to industrial furnaces³⁻⁵.

Controlled combustion, which occurs at conditions of high preheat and low O_2 concentration, is the result of chemical processes which are fundamentally different from conventional combustion processes. Detailed kinetic models, which are currently optimized for conventional combustion, are needed to model implementation of controlled combustion in low-irreversibility engines. Development of an engine that utilizes controlled combustion will rely heavily on detailed kinetic models developed and validated specifically for these conditions. Since the engine combustion process would occur at elevated pressure, the influence of pressure on the reaction kinetics should also be investigated.

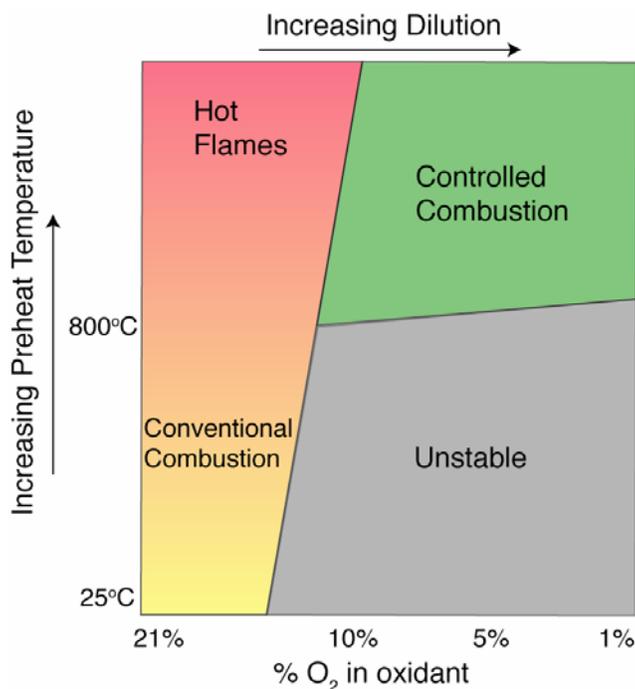


Figure 1: The regimes of combustion with variations in O_2 concentration and preheat temperature.

Background

Figure 1 shows the regimes of combustion processes as determined by preheat temperature and the concentration of O_2 in the oxidant mixture, with controlled combustion occurring at low O_2 concentration and high air preheat. Controlled combustion is being experimentally investigated in a high pressure flow reactor facility where these parameters, along with fuel composition and concentration, can be varied independently at pressures up to 50 bar and temperatures up to 1400 K. This facility, shown in Figure 2, has been developed specifically for the investigation of combustion chemistry at high pressure.

The conditions in the reactor are monitored using various probes. The temperature field in the reactor is measured using a thermocouple and gases in the reactor are sampled by extraction through a water-cooled quartz probe. Concentrations of key reactant, intermediate, and product species in the sample gas are measured online. The measured concentration profiles can be compared with profiles predicted by detailed reacting flow models.

The reaction mechanism used to analyze the experimental data, GRI-Mech 3.0, was developed by the Gas Research Institute for conventional combustion of natural gas⁶. This model, which includes 325 elementary reactions among 53 species, is used in combination with codes from the CHEMKIN-III⁷ suite.

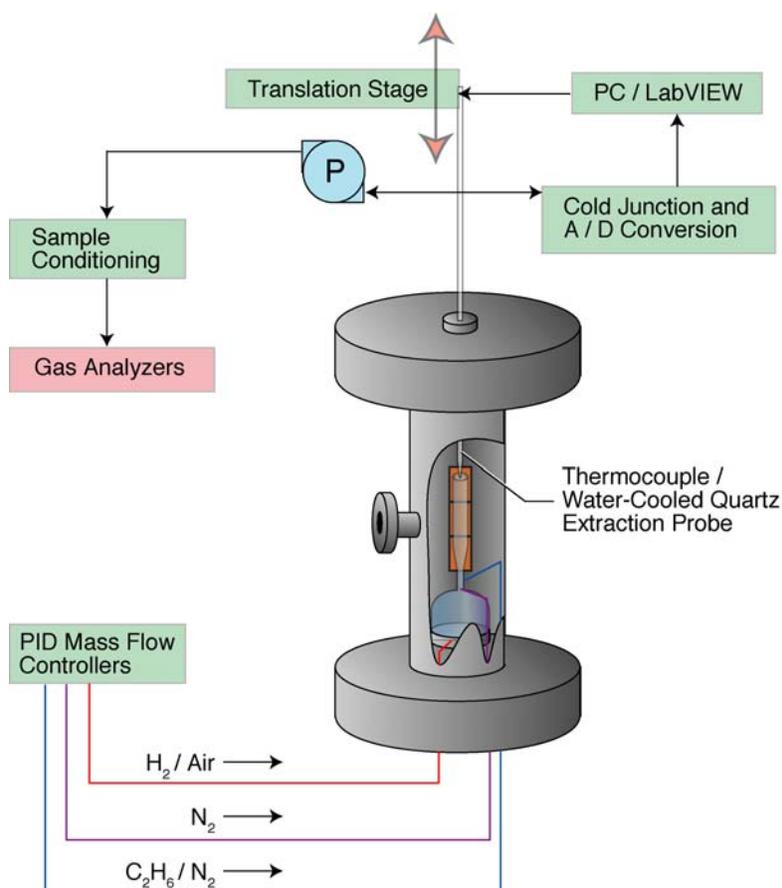


Figure 2: Schematic of the flow reactor in the high-pressure facility.

Results

Studies were conducted using ethane, methane and methane-ethane mixtures to simulate natural gas. Figures 3 through 5 are representative comparisons of the experimental data and model results for ethane.

Comparisons of measured profiles of stable species concentrations and temperature for controlled combustion of C_2H_6 at ambient pressure with predicted profiles are shown in Figures 3 and 4 for a pressure of 1 bar. Figure 5 shows this comparison for a pressure 2 bar. Measured and predicted temperature, O_2 and CO_2 profiles are in good agreement in all of the experiments; however, discrepancies between the measured and predicted profiles of the fuel, C_2H_6 , and C_2H_4 and CO are observed. In addition to C_2H_4 , trace amounts of CH_4 are observed; both of these species are products of the initial stages of the fuel oxidation reaction. One significant feature of the fuel oxidation process is that the oxidation rate decreases as pressure increases, a result not observed under normal combustion conditions for small hydrocarbons.

To determine the reactions that are important in initial fuel oxidation and CO formation, sensitivity analyses were carried out using Senkin⁸. Two features of the CO profile were used in these analyses – the time-to-peak CO concentration and the half-width of the CO profile. Representative results from these sensitivity analyses are

shown in Figures 6 and 7. For the conditions of the experiments in Figures 3 – 5, reactions involving the peroxy radical, HO_2 , are among the most important in the initial fuel oxidation. Because of the relative stability of this radical, its role in the reaction mechanism tends to be inhibitive. At a pressure of 2 bar, predicted HO_2 levels are higher than at a pressure of 1 bar, which is a partial explanation for the decreased reaction rate with increasing pressure. The rate parameters for many of the reactions involving HO_2 in the starting oxidation mechanism have relatively large uncertainties, and this is an area for future improvement of the mechanism.

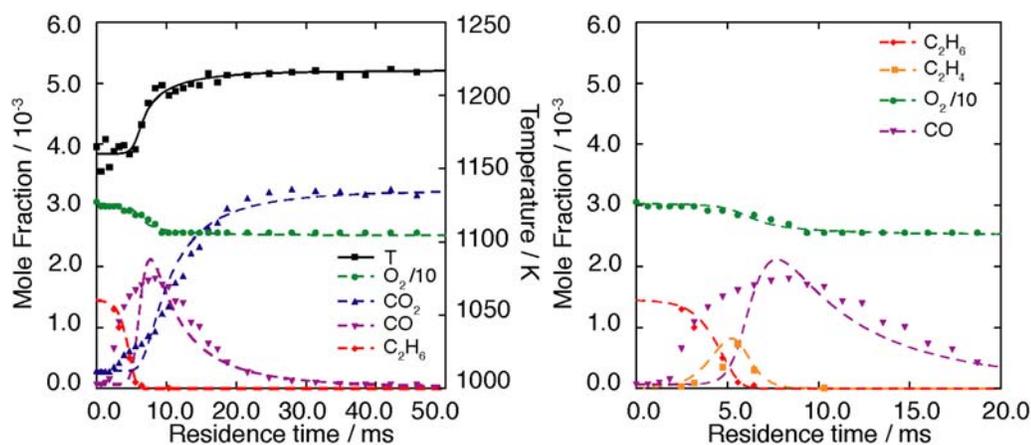


Figure 3: Comparison of measured and predicted time profiles of temperature and stable species. Pressure = 1 bar; initial temperature=1170K; 1500 ppm C_2H_6 ; 3.0% O_2 .

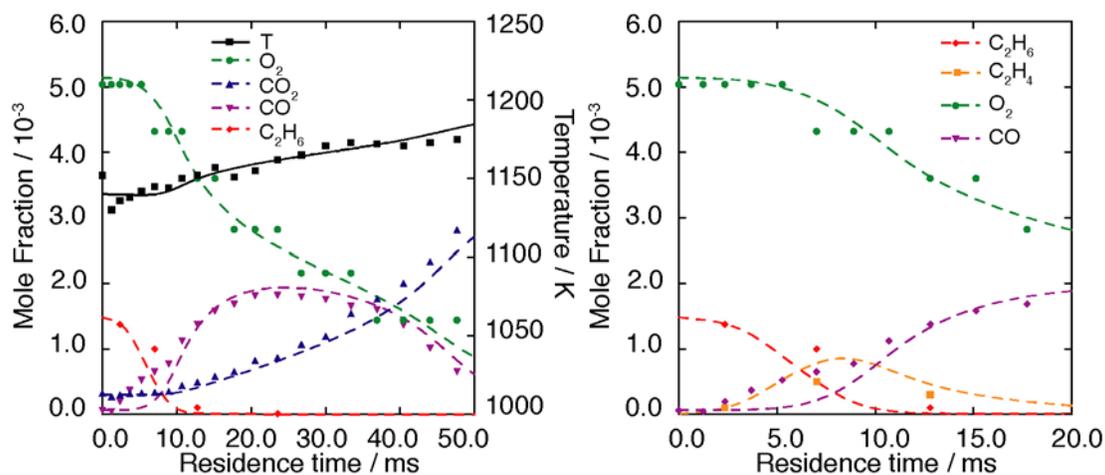


Figure 4: Comparison of measured and predicted time profiles of temperature and stable species. Pressure = 1 bar; initial temperature = 1150K; 1500 ppm C_2H_6 ; 0.5% O_2 .

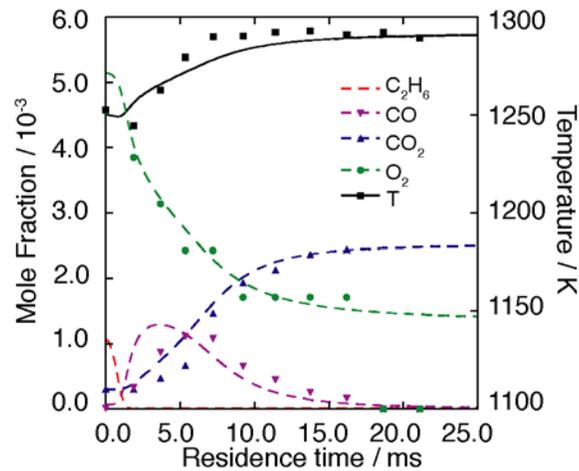


Figure 5: Comparison of measured and predicted time profiles of temperature and stable species. Pressure = 2 bar; initial temperature = 1250K; 1050 ppm C₂H₆; 0.5% O₂.

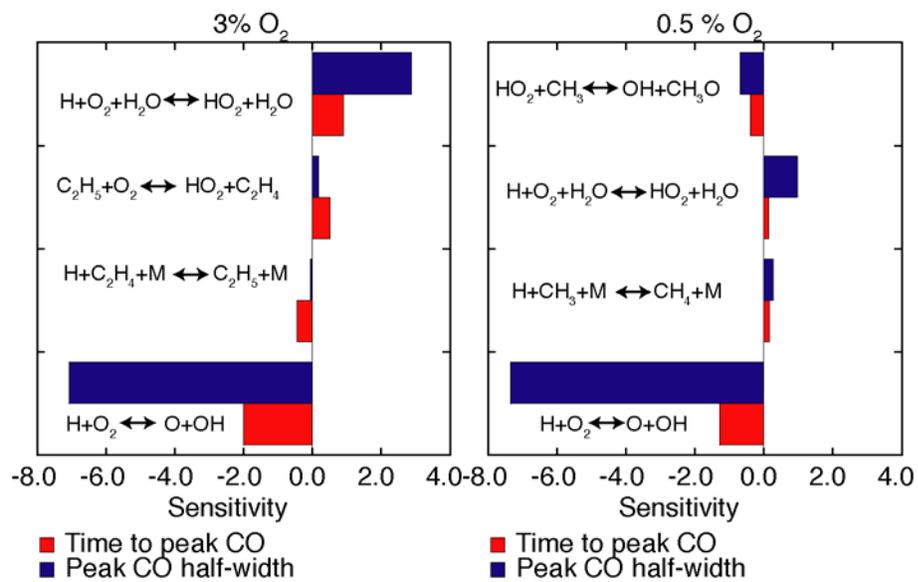


Figure 6: Results from sensitivity analysis for CO for the conditions of Figure 3 (left) and Figure 4 (right).

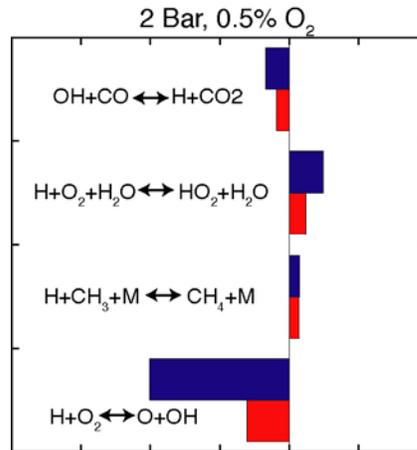


Figure 7: Sensitivity analysis for CO for the experimental conditions of Figure 5.

Figure 8 shows measured and predicted temperature profiles for ethane and methane at the same initial temperature and O₂ concentration. The oxidation rate for methane under these conditions is significantly slower than for ethane. The agreement between measured and calculated temperature profiles is good.

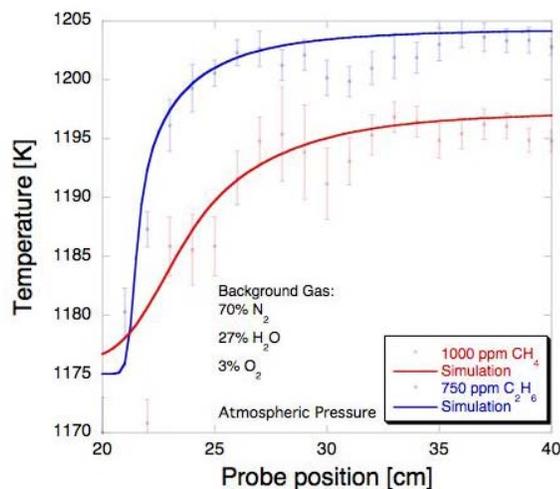


Figure 8: Comparison between measured and calculated temperature profiles for methane and ethane.

Conclusions

Controlled combustion of ethane and methane has been demonstrated in the flow reactor. The data obtained indicate that the combustion reaction can be inhibited sufficiently such that the combustion process can be spread over tens of milliseconds. Initial model predictions show reasonable agreement with the measured temperature, CO₂ and O₂ profiles. However, predicted CO and stable hydrocarbon species profiles are significantly delayed compared to the experimental profiles. Sensitivity analyses have identified reactions of the hydroperoxyl radical, HO₂, as important elementary reactions that impact the initial stages of the reactions and, given that the rate parameters of these

reactions are uncertain, some refinement of the chemical model will be required for accurate predictions of controlled combustion.

The implication of the results is that by carefully controlling the temperature and composition of the reactants, the rate at which fuel and oxygen react can be tailored so that heat release and expansion rates can be matched. This offers a potential for reducing irreversibilities and increasing the efficiency of energy conversion devices, resulting in fuel savings and decreased emissions of CO₂.

Future work should focus on implementation of the controlled combustion concept in laboratory-scale energy conversion devices.

Publications

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