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Poster #

Autoignition delay measurements in syngas and natural gas at sCO_2 conditions

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ABSTRACT

The direct-fired supercritical CO_2 (sCO_2) cycles promise high efficiency and reduced emissions while enabling complete carbon capture. However, there is a severe lack of fundamental combustion kinetics knowledge required for the development and operation of these cycles, which operate at high pressures and with high CO_2 dilution. Experiments at these conditions are very challenging and costly. In this study, a shock tube was used to investigate autoignition tendencies of several mixtures under high carbon dioxide dilution and high fuel loading. Individual mixtures of oxy-syngas and oxy-methane fuels were added to CO_2 bath gas environments and ignition delay time data was recorded. Reflected shock pressures neared 100 atm, above the critical pressure of carbon dioxide in to the supercritical regime.

INTRODUCTION

In this study, synthesis gas (syngas, mixture of H_2 and CO) and methane gas (as a surrogate for natural gas) were investigated as fuels for the direct fired sCO_2 cycle. This study provides new ignition delay time (IDT) data at high pressures around 100 atm, in oxy-methane and oxy-syngas mixtures in a shock tube with high CO_2 dilution up to about 92% and at various equivalence ratios near stoichiometric conditions (φ). The dilution rates and pressure ranges are relevant to direct-fired combustor designs, most importantly, these experiments help the development of chemical kinetic mechanisms. Also, this research investigated changes in θ, the fuel ratio of hydrogen-to-carbon monoxide as well as different fuel loadings. Fuel loading is defined as the mole fraction summation of all fuels and oxidizers. In total, five mixtures were investigated with a pressure range of 70-100 atm and a temperature range of 1050-1350K. Additionally, we compared the performance of two widely used chemical kinetic mechanisms against current data. To our knowledge, we report the first ignition data for the selected mixtures at these conditions. The experimental data presented here will be used in the development of chemical kinetic mechanisms while the performance comparisons provide some suggestions on areas of attention on existing mechanisms and their accuracy under these conditions.

EXPERIMENTAL SETUP

The experiments performed in this study were taken with one of the stainless-steel, double-diaphragm, heated shock tube at University of Central Florida (UCF) with an internal diameter of 14.2cm. The driven and driver sides were separated with a combination of polycarbonate Lexan diaphragms and 1018 steel metal diaphragms in a double diaphragm design. The driven side is vacuumed to at least 5.0×10^{-5} Torr before being filled with a specific pressure of a pre-

made gas mixture in a separate tank. The driver side was filled with helium until the diaphragm or diaphragms ruptured causing a shock wave to form, which quickly traveled down the driven side of the shock tube. Five piezoelectric pressure transducers (PCB 113B26) placed along the last 1.4 m of the driven section of the shock tube are connected to four time-interval counters (Agilent 53220A) to measure the shock velocity.

The shock tube setup is shown in Figure 1. In this figure, the shock wave was formed near the diaphragm after rupturing and travels down the length of the driven section. Once this shock wave hits the end-wall it reflects, yielding test conditions (T_5 and P_5) shown in red. Details about shock tube and operation can be found in our earlier work [1-6])

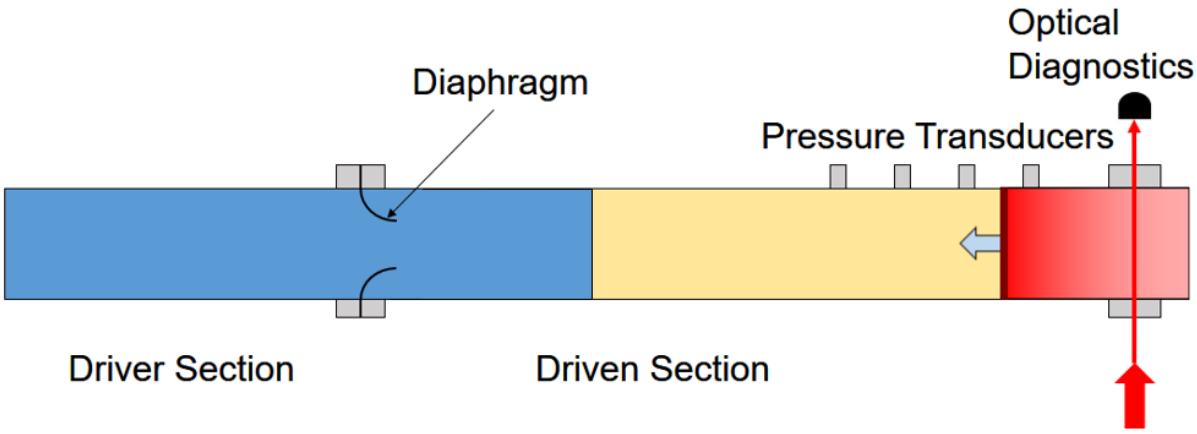

Figure 1. The shock tube system after the shock wave has reflected off the end-wall.

Each mixture was prepared manometrically in a 33L Teflon-coated, heated, stainless-steel mixing tank. Mixtures were made from research grade gases (> 99.999% purity) supplied by nexAir. The pressure was measured using a 100 Torr (MKS Instruments Baratron E27D) and a 10,000 Torr (MKS Instruments/Baratron 628D) full scale range capacitance type manometers. The tank was left to mix for at least eight hours with a magnetically driven stirrer to ensure homogeneity. At the time of the experiment, the mixture was then introduced into the shock tube.

The reflected shock wave temperature (T_5) and pressure (P_5) were calculated using the measured shock velocity (V_s), initial pressure (P_1) and temperature (T_1) data employing the ideal shock relations and thermodynamic properties of the mixture [7]. Non-ideal gas concerns were investigated in [8] and found at most 5% deviation from ideal laws. The average uncertainty of temperature and pressure have been calculated to be around 1%. The vibration relaxation time, discussed in further detail later in this paper, was calculated for each mixture to ensure that these test conditions (T_5, P_5) were realized quickly before ignition measurements were taken. Data were recorded using an NI PCI-6133 Data Acquisition Device at 2MHz per channel. At 2 cm from the end-wall of the driven section, measurements were taken from radial ports. Pressure measurements were obtained using a dynamic piezoelectric pressure transducer (Kistler 603B1). Another port contained a sapphire window which allowed light emissions to be recorded. Either a GaP transimpedance amplified detector (Thorlabs PDA25K, sampling frequency between 15MHz- 6.6kHz) operating in the wavelength range between 150 and 550 nm or a Large Area Optical Receiver (Newport 2032, sampling frequency between 1.8 MHz-300 kHz) operating in the wavelength range between 190 and 1110 nm was used. This detector was

operated without the use of any bandpass filters to achieve high signal-to-noise ratio to measure the emissions from combustion. It has been previously shown that CO_2 dilution reduced the overall emissions from combustion [5], therefore, signal to noise was a concern in emission data. Most of the light emissions of the experiment are coming from the ignition event associated with OH*, the excited OH radical found in all combustion experiments, or additionally CH*, the excited CH radical found in all hydrocarbon combustion experiment. Since OH* and CH* trend well together, these were assumed to be homogenous emissions for the methane mixture [9]. In **Error! Reference source not found.**, it is shown that these emissions correspond well with the ignition event compared to the steep rise in the pressure trace. Since the emissions trace was normalized, it is noted that there were proportionally negligible emissions from other species (e.g., CO_2, H_2O) that could interfere with proper determination of the ignition event.

RESULTS AND DISCUSSION

The experiments shown in Figure 2 of Syngas were predicted well by the Aramco 2.0 mechanism, although with some slight disagreement with an experiment in the colder regime.

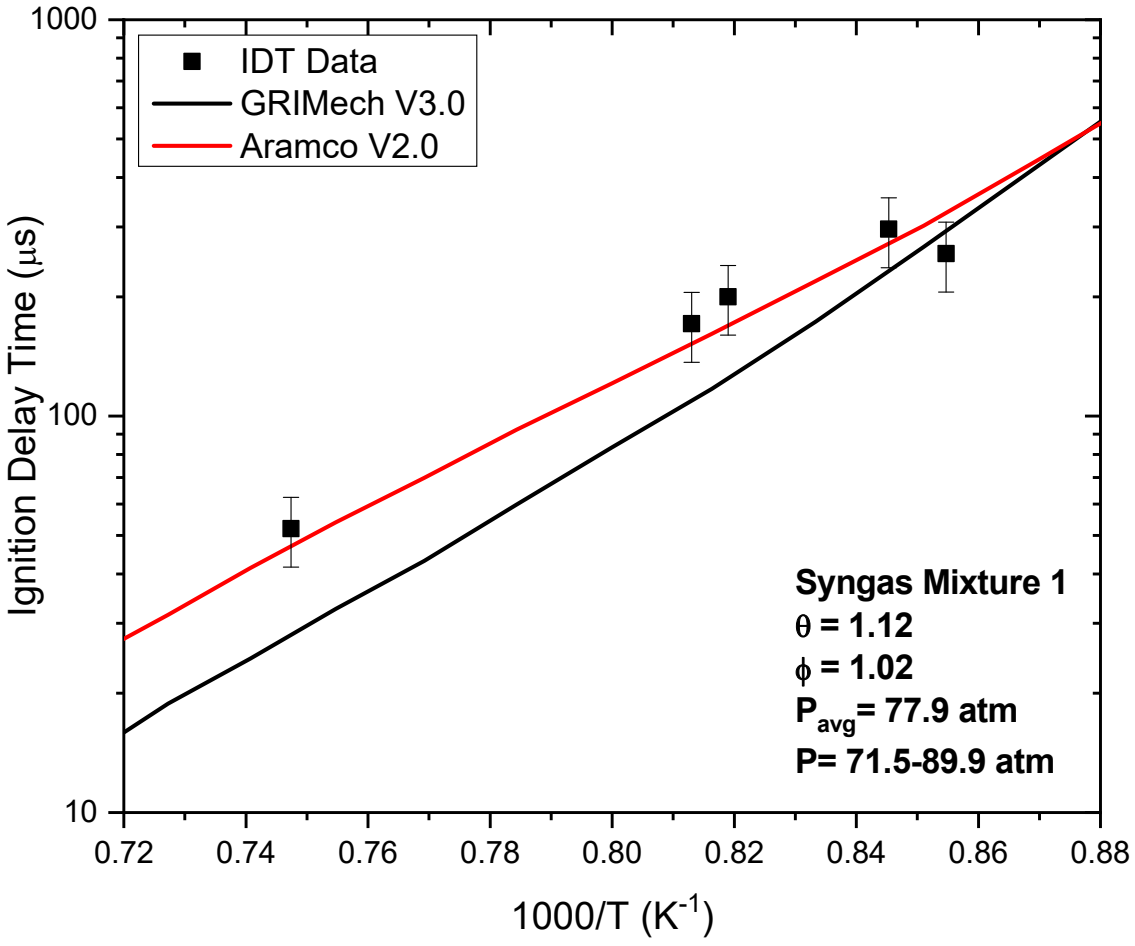

Figure 2. Experimental syngas ignition delay times and comparisons with predictions of two mechanisms (θ = 1.12 and φ = 1.02). The mechanisms were run at the average pressure of 77.90 atm.

The overall profile of a reduction of the ignition delay time as temperature increased was well captured. The vibrational relaxation time of this mixture was calculated and had maximum time of 1.11 µs. This relaxation time is very minor compared to the measured ignition delay times. GRI V3.0 did not perform very well at these predictions. The mixture was designed to simulate conditions in the center of the combustor and had a near stoichiometric equivalence ratio (additionally, this had low fuel loading). The Aramco 2.0 mechanism can accurately model current experimental data over all these conditions tested.

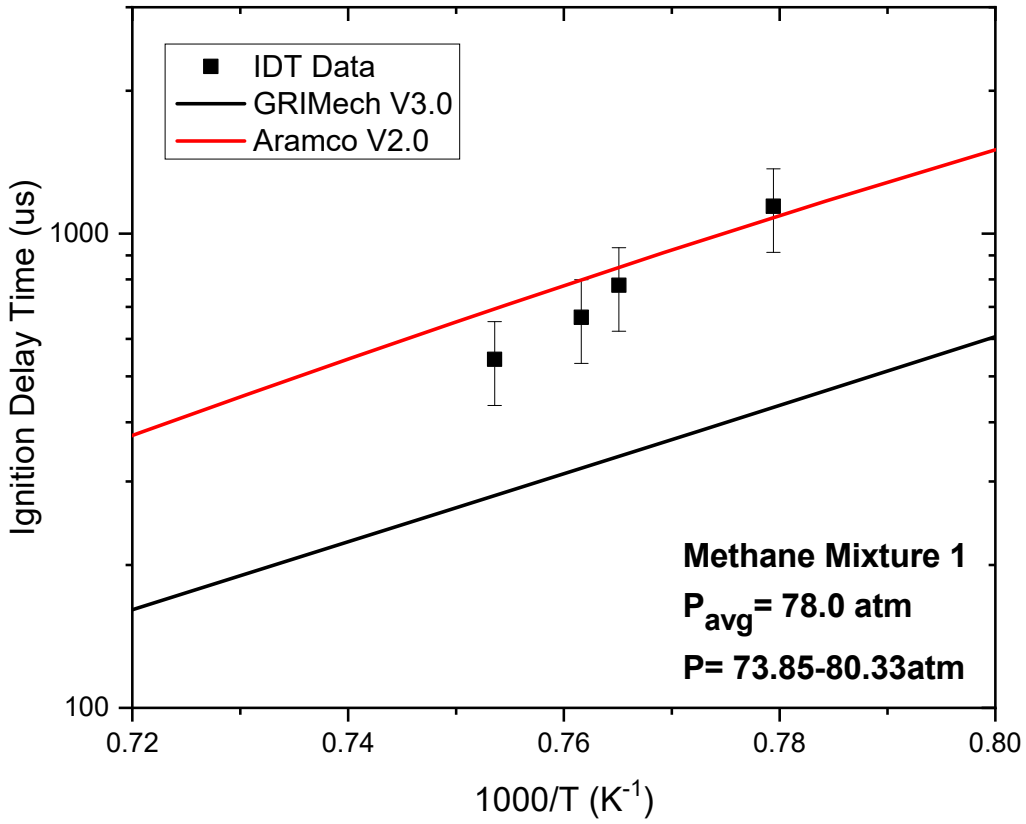

Figure 3. Experimental methane ignition delay times and comparisons with predictions of two mechanisms. The mechanisms were run at the average pressure of 78.0 atm. This mixture contains 4.5% CH_4/ 9% O_2/36.5%CO2/ 50% N2.

Experiments were performed around 80 atm for methane oxidation in a CO_2 diluted environment. The mixture was diluted with nitrogen to prevent detonation pressures that could exceed material limits behind the reflected shock wave. The maximum relaxation time of this mixture was calculated to be 6.6 µs with available literature. This relaxation time is very minor compared to the ignition delay times reported (> 300 µs). Methane relaxes itself within 0.03 µs seen though other relaxation parameters were not available in literature molecules. Since methane has more than 3 atoms there are several degrees of freedom and other molecules interacting with methane will further reduce the relaxation time of the mixture.

The ignition delay times were measured using the slope of the emissions profile for all these experiments. The temperatures and pressures reported are before ignition occurs. Predictions by the Aramco 2.0 mechanism showed very good agreement with current data. At hotter temperatures, there is a deviation and the measured ignition delay time was shorter than the simulated ones. The GRI V3.0 mechanism did not perform very well at these conditions. The model underpredicted the ignition delay times throughout the entire temperature range. The

mixture was designed to simulate conditions at stoichiometric equivalence ratio and low fuel loading. Similar observations regarding the Aramco 2.0 mechanism performance for methane were reported earlier at a range of pressures including the supercritical CO_2 conditions [22]. However, for syngas it is a different story [24, 27] and thus the current and future investigations will focus on more syngas mixtures

ACKNOWLEDGMENTS

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