A Study on Ignition Delay Times of Methane/Ethane Mixtures with CO₂ and H₂O addition

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1 Introduction

The global energy demand is expected to increase substantially within the next 20 years; for example, by more than 25% to 2040, as modeled in the New Policies Scenario in the World Energy Outlook 2018 of the International Energy Agency [1]. Thus, extensive efforts will be assigned to improvements of existing combustion concepts and to the development of new approaches for heavy duty gas turbines. The ultimate goal is to minimize the harmful environmental effect with e.g. NOx and CO₂ emissions. In the energy roadmap 2050 [2] of the European Commission electricity plays a pivotal role, with the prospect of almost totally eliminate CO₂ emissions, to counteract climate change; Carbon Capture and Storage (CCS) is seen as a central low-carbon technology to achieve the GHG emission reduction objectives.

Oxy-fuel combustion is the process of burning a fuel in pure oxygen instead of in air, with no nitrogen present. This technique has attracted much interest in firing fossil-fueled power plants as it has practically no NOx emissions. The combustion products are water (H_2O) and CO_2 which can be captured and sequestered [3-5] by separating the water. However, higher flame temperatures are achieved. To account for, the fuel mixture is diluted by mixing with diluents such as CO_2 and other recycled flue gas to replace nitrogen in the cycle to maintain cycle efficiency. Thus, reduced CO_2 emissions will be realized through re-circulating the exhaust stream back into the system. For example, oxy-combustion natural gas stationary power cycles employing up to 90%/vol. CO_2 have been proposed [6]. To foster their commercial implementation, accurate fundamental knowledge with respect to the effects of H_2O and CO_2 is needed.

In this study, ignition delay times of RefGas, a natural gas surrogate consisting of 92% methane (CH₄) and 8% ethane (C₂H₆) [7], will be examined under oxy-fuel conditions including addition of H₂O, for the first time, to the best of our knowledge. In the past, the effects of CO₂ on methane in an oxy-fuel environment has been studied focusing on flame speeds of nitrogen diluted mixtures to CO₂ mixtures and on ignition delay times [8-10]. For example, it was found that CO₂ addition reduces the flame speeds compared to air due to the difference in the heat capacity compared to N₂ [8] and due to the competition between CO₂ and oxygen (O₂) for H radicals reducing the radical pools and inhibiting the overall reaction rate. A more detailed overview is given in [11].

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2 Approach - Experimental and Modeling

Experimental

The experiments were performed at two different shock tube facilities. Ignition delay time data of the mixtures selected (stoichiometric mixtures, $\varphi = 1.0$; for details, refer to Table 1) were measured at temperatures ranging between about 800 and 1600 K and at total pressures of about 16 ± 2 bar.

Mixture	X _{CH4}	X _{C2H6}	X _{O2}	X _{CO2}	X _{H2O}	Facility
1	0.1451	0.0126	0.3289	0.5134	0.0000	UCF / DLR
2	0.0767	0.0067	0.1667	0.7000	0.0500	UCF
3	0.0759	0.0075	0.1669	0.6498	0.1000	UCF
4	0.0758	0.0081	0.1680	0.5983	0.1498	UCF
5	0.0726	0.0063	0.1645	0.2567	0.5000	DLR
6	0.0726	0.0063	0.1645	0.7567	0.0000	DLR

Table 1: Summary of stoichiometric mixtures studied; mole fraction of species given.

The DLR shock tube used has an internal diameter of 4.60 cm and was pumped down before each experiment using a turbo molecular vacuum pump, to pressures at about 10^{-5} mbar (driven section). The gaseous mixtures were mixed several days before use except at the highest water load where every mixture was prepared by water injection followed by 15 minutes stirring at 160 °C before each shock. The partial pressure method was used to determine the composition of each mixture. All gases used for the experiments were lab grade gases (>99.999% purity). The driven section of the shock tube was kept at a constant temperature of 160 °C and the driver section at 120 °C, respectively throughout the experiments. The temperature and pressure behind the reflected shock wave were computed from the measured incident shock speed, with the speed attenuation calculated using a one-dimensional shock model. For a more detailed description of the high pressure shock tube, see ref. [12]. Ignition delay times were determined using a Hamamatsu R3896 photomultiplier tube by measuring the CH* emission at 431 nm isolated by narrow band pass filters (Hugo Anders, FWHM ≤ 5 nm) and amplified by a FEMTO HLVA-100 logarithmic amplifier. The pressure was measured using a Kistler 603B pressure transducer shielded by an RTV106 high temperature silicone rubber coating to eliminate thermal shock to the transducer. Both devices were located 10 mm from the end wall (Fig. 1 (a)). Furthermore, ignition delay times were corrected by an experimentally derived blast-wave propagation time delay and compared for validation at the highest temperatures within each series to the end plate emission characteristics. The experimental setup allowed measurements of ignition delay times up to 10 ms depending on the temperature and the gas mixture. In addition to the radial measurements, axial emission was detected spectrally resolved to 5 different wavelengths (310 nm, 375 nm, 431 nm, 473 nm and 516 nm; FWHM \leq 5nm) through a sapphire window in the end wall.

The UCF shock tube has an internal diameter of 14.2 cm [8] and was evacuated before each experiment using a turbomolecular vacuum pump. The driven section was kept at a constant 100 °C throughout the driven section length. Ignition delay times were measured using a PDA25K photodetector from Thorlabs. A narrow bandpass filter at 310 ± 10 nm was used to isolate the hydroxyl radical (OH*) emission. A 430-nm filter (CH*) was also tested to compare results for the initial rise described in the high-water concentration mixture although there was little difference between the results of the two filters. The pressure (p_5) was measured using a Kistler 603B1 pressure transducer. For more details on the UCF shock tube, see Koroglu et al. [8]. The shock velocity was calculated using 5 PCB 113B26 pressure transducers

located along the last 1.4 m of the driven section. The pressure transducers were attached to four Agilent 53220A timer-counters to accurately record the passage of the incident shockwave. The velocity was then used to calculate pressure and temperature behind the reflected shock wave; with an uncertainty of temperature and pressure less than 2.5%. Each mixture was created using a 33 litre mixing tank using lab grade gases (>99.999% purity). De-ionized water was injected first and allowed to vaporize before injecting other gases. The mixing tank pressure was monitored using a 10000 torr MKS baratron (628D). Mixing tank and manifold were heated to a constant 135 °C throughout the experiments.

Modeling

Numerical simulations of shock tube data were performed using a closed-homogeneous batch reactor with constant-volume and constant-internal energy assumptions as enclosed within the Chemkin Pro software package [13]. The Aramco 2.0 mechanism [14] with 493 species and 2716 reactions involved was used augmented by a CO_2^* sub model taken from Kopp et al. [15]. The calculations were done at $p_{init} = 16$ bar with a facility dependent pressure profile derived from the low temperature shocks of DLR's experimental data (see Fig. 4 – insert, up to 8 ms). Note that this pressure rise mainly affects the longer ignition delay times in the high fuel loading mixture as experiments lasted as long as 20 ms and this lowers the ignition delay times at the lower temperatures as can be seen in Fig. 4.

3 Results and Discussion

Experiments were done for mixtures of oxy-RefGas diluted with carbon dioxide and water at a constant pressure $p = 16 \pm 2$ bar and temperatures ranging between 800 and 1500 K. The experimental ignition delay time was defined as the time between the arrival of the reflected shock wave at the end plate to the peak of the emission signal. The arrival of the reflected shock wave was determined as follows: (i) at the DLR facility, by calculating the velocity of the incident shock wave and extrapolating from the arrival of the incident shock wave at the end plate; and (ii) at the UCF facility, through both laser absorption schlieren which coincided with the midpoint of the reflected shock pressure rise. The Schlieren spike from 3.4 µm laser was used to determine time-zero [8].

First, experiments were performed in both shock tubes to recreate experimental conditions for Mixture 1 (fuel/O₂ with only CO₂ present as diluent) at both facilities. The ignition delay times are within the margin of error between the two facilities as can be seen from Fig. 1 showing the comparison between two experiments conducted at $T \approx 1210$ K. The major difference is the higher post ignition pressure rise that was noted at UCF; however, the ignition delay times for the experiments differed only by 20 µs (well within the uncertainties ± 20%).

Effect of CO₂ Dilution on RefGas Ignition Delay Times

Figure 2 shows the data taken for Mixture 1 compared to the predictions of the Aramco 2.0 mechanism. The large scatter in the experimental data points is boosted by the high fuel-oxidizer loading chosen to be 50% of the mixture. Intentionally reaching as low an ignition temperature as possible this is exacerbating any effects that may dominate chemical kinetics at these lower temperatures caused for example by boundary layer effects or membrane burst. However, important trends are still able to be drawn.

A good match between measured and calculated data is seen at higher temperatures above 1200 K. Although the pressure rise was considered in the simulations, for temperatures around 1250 K or below, the Aramco 2.0 mechanism still overpredicts the ignition delay times by factors of about 2 to 4.

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The findings of the present work shows the same temperature behavior when comparing with the results reported previously for pure methane [9], where the reaction models were able to accurately predict the ignition delay times for temperatures above 1300 K. This study is the first one reporting on ignition delay time measurements of a natural gas surrogate at such low temperatures where the chemistry that would dominate the combustion process could be quite different to the high temperature chemistry [16]. At higher temperatures, most hydrocarbons tend to follow similar decomposition pathways and ignition delay times collapse upon each other. It is only in the low temperature regions that major difference can be observed in the fuels.



Figure 1. Pressure and side on emission profiles for a sample experiment of Mixture 1. (a) DLR. (b) UCF.



Figure 2. Comparison between measured (symbols) and calculated (curves - Aramco 2.0) ignition delay times of Mixture 1 calculated with p=p(t).

Effects of Water and Carbon Dioxide Dilution on RefGas Ignition Delay Times

Experiments were performed for several mixtures (Mixtures 2-6 in Table 1) to look at the combination of the diluents H_2O and CO_2 on the effect of ignition delay times of RefGas. The comparison between experimental and predicted ignition delay time data show a good match for the Mixtures 2-4, with an increased level of water up to 15%, and oxidizer loading of 25%; see exemplarily for M3 (Fig. 3). This result is similar to the one of the study on ignition delay times of highly diluted CO_2 methane mixtures [9]. Thus, recirculation of the exhaust gas to reduce emissions of natural gas combustion appears viable.

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Figure 3. Comparison between measured (symbols) and calculated (curves, Aramco 2.0) ignition delay times for Mixture 3.

Figure 4. Comparison between measured (symbols) and calculated (curves, Aramco 2.0) ignition delay times for Mixtures 5 and 6. Insert: pressure profile $p / p_{init}(t)$.

To understand the effect that water would have on RefGas ignition and to stress the chemical kinetics, experiments were performed with 50% H₂O addition to Mixture 1, i.e. only 25% CO₂. Their determined ignition delay time data (Mixture 5, Fig. 4) are longer, by about a factor of 2 to 3, than those predicted by the Aramco 2.0 model, within the temperature range studied, i.e. between 1100 and 1500 K. The same behavior was found for Mixture 6, with additionally 50% CO₂ (compared to M5) addition, i.e. 75% CO₂ in total and without water (Fig. 4). Therefore, a sensitivity analysis was performed on ignition delay times are found to be similar to those for Mixture 2. The difference between various reactions are changes in the C2 chemistry with H₂O playing some role. Furthermore, the predictions suggest an acceleration of the ignition process in the presence of water compared to CO₂, whereas the experiments only indicate no effect.



Figure 5. Axial emission profiles at different wavelengths (308 nm, 375 nm, 431 nm, 473 nm, 516 nm) of M5 and M6: Immediate rise after arrival of reflected shock wave before ignition (not seen in 50%CO₂/50% H₂O - mixtures).

The experiments further revealed that at elevated temperatures the emissions exhibited a large initial rise shortly after the arrival of the reflected shock (Fig. 5). The emission profile was seen at several different wavelengths in the visible light spectrum but not at 308 nm (for measuring OH* for ignition determination). A suggestion is that CO_2^* was being formed resulting in a small amount of emissions immediately after the arrival of the reflected shock wave. This phenomenon is only present with the addition of the fuel and oxidizer, but was not present shock heating CO_2 / water – mixtures without fuel. This indicates that the reactions leading to involving CO_2^* are becoming more relevant at elevated **27th ICDERS – July 28th - August 2nd, 2019 – Beijing, China** 5

temperatures and are playing a larger role in the combustion process diagnostics than was previously understood.

4 Summary and Conclusions

Ignition delay times were measured for several mixtures covering high fuel loading of RefGas, a natural gas surrogate, with CO_2 and H_2O added as diluents being the first experiments conducted under these oxycombustion conditions and the lowest temperature ignition delay times for this type of fuel. The results show that the Aramco 2.0 model overpredicts ignition delay times for high fuel/oxidizer loaded mixtures. For low levels of water addition (up to 15%), the Aramco 2.0 mechanism is able to accurately predict the ignition delay times. However, at high water (50%) and CO_2 levels, the measured ignition delay times are underpredicted. These experiments also resulted in a unique emission profile assigned to CO_2^* , with an immediate rise in the axially measured emission signal detected after the arrival of the reflected shock wave. Experiments illustrate that the emission profile only occurs in the presence of fuel. A baseline of 50% water and 50% CO_2 was also examined with no emission detected. Future experiments will focus on understanding how water affects the combustion process at different pressures and understanding the emissions and species profiles in an oxy-fuel environment.

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