Shock Tube Study of the Ignition of Lean CO/H₂ Fuel Blends at Intermediate Temperatures and High Pressure

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1 Introduction

The study of the combustion characteristics of H_2/CO fuel blends is of fundamental and technical interest because the H_2/CO system is very important in the hierarchical structure of oxidation models of hydrocarbon fuels and in advanced combustion technologies such as Integrated Gasification Combined Cycle (IGCC) which are currently developed allowing a reduction of the emissions of the power generation using biogenic sources and coal as fuel. In the IGC cycle 'syngas' which contains mainly H_2 and CO is produced by the gasification of coal, municipal waste or biomass. It is further processed by subsequent separation of pollutants and sequestration of CO_2 before its combustion in gas turbines. For the development of the 'syngas' combustors the characteristics of the H_2/CO systems must be understood.

2 Experimental setup

The experiments were carried out in a high pressure shock tube with an internal diameter of 98.2 mm. It is divided by aluminium diaphragms into a driver section of 5.18 m and a driven section of 11.12 m in length. The driven section can be pumped down to pressures below 10^{-6} mbar by a turbomolecular pump. Gas mixtures were prepared manometrically in a stainless steel storage cylinder, which is evacuated using a separate turbomolecular pump to pressures below 10^{-6} mbar. The shock speed was measured over three intervals using four piezo-electric pressure gauges. The temperature and pressure behind the reflected shock wave were computed from the measured incident shock speed and the speed attenuation using a one-dimensional shock model. The estimated uncertainty in reflected shock temperature is less than ± 15 K in the temperature and time range of our measurements. The purity of the used oxygen was better than 99.9999%, of argon better than 99.9999% and of carbon monoxide better than 99.9997%.

The ignition was observed by measuring pressure profiles with piezo-electric gauges (PCB 113 A24) located next to the end flange. Also, the OH* emission at 307 nm at the same position was selected by a narrow band pass filter (FWHM = 5 nm) and measured with a photomultiplier. All ignition delay time values shown in these report were determined by measuring the time difference between the initiation of the system by the reflected shock wave and the occurrence of the OH* maximum.

The experimental setup allows measurements of ignition delay times at constant pressure and temperature condition for observation times < 4.5 ms.

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3 Results

The ignition delay times of 6 different H₂/CO/O₂/Ar-mixtures (fuel: 5% H₂ / 95% CO, $\phi = 0.5$, dilution 1:2, 1:5, 1:10, fuel: 50% H₂ / 50% CO, $\phi = 0.5$, dilution 1:2, 1:5, 1:10) were measured at pressures of about 16 bar and temperatures between 1020 and 1260 K. Typical results are presented in Fig. 1a and 1b.

Figure 1a shows an experiment with 50% $H_2 / 50\%$ CO and a dilution of 1:10 at T = 1054 K and p = 15.59 bar. A strong increase of the pressure and the emission can be observed at about 4000 µs. Similar characteristics of the signals are found for both H_2/CO mixtures at dilutions of 1:2 and 1:5 and for the 50% $H_2 / 50\%$ CO fuel blend at a dilution of 1:10 at temperatures lower than 1100 K with the pressure increase becoming weaker with increasing temperature for this mixture. A slow increase of the pressure and the emission before strong ignition could be observed only for the experiments with the 5% $H_2 / 95\%$ CO mixture at a dilution of 1:5.

The 5% $H_2 / 95\%$ CO fuel blend at a dilution of 1:10 shows two emission maxima (see Fig. 1b). The first one is increasing relatively to the second one with increasing temperatures. The pressure profiles feature a continuous small increase during the observation time beginning with the first maximum in the OH* emission but no steep increase and no maximum.



Fig. 1: Typical pressure and OH* emission profiles of lean H₂ / CO / O₂ / Ar mixtures ($\Phi = 0.5$, dilution 1:10, fig 1a: 50% H₂ / 50% CO, T = 1054 K, p = 15.6 bar; fig. 1b: 5% H₂ / 95% CO, T = 1223 K, p = 16.0 bar).

4 Discussion

The measured ignition delay times and comparisons to predictions of literature mechanisms (GRI3.0 [1], LEEDS1.5 [2], Davis et al. [3], Li et al. [4]) are summarized in fig. 2 (5% $H_2/95\%$ CO) and fig. 3 (50% $H_2/50\%$ CO)). The reaction H + O + M \Leftrightarrow OH* + M and thermal and spectroscopic relaxation reactions of OH* were added to the mechanisms for comparability with the experimental results.

The model of Davis et al. [3] agrees very well with the measurements of the 5% H_2 / 95% CO fuel blend in the whole temperature range of this study. For the lowest temperatures considered for this mixture (dilution 1:2) the simulations with the GRI3.0 [1] and the LEEDS1.5 [2] mechanisms also reproduce very well the experimental results. For higher temperatures (dilutions 1:5 and 1:10) they predict clearly too long ignition delay times. The simulations with the model of Li et al. [4] show

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generally too long ignition delay times, especially at lower temperatures. The double peak structure and the very broad OH*-emission profiles of the 5% H₂/95% CO mixture with a dilution of 1:10 (see fig. 1b) are qualitatively well described by all mechanisms used. The OH*-maxima are caused by maxima in the H- and O-concentration profiles, leading to the production of OH* by the reaction of O+H \Leftrightarrow OH*. The first maximum appears during the fast oxidation of the H₂, which initializes the CO oxidation causing a second OH*-maximum. For the less diluted mixtures the temperature increase by the H₂-oxidation is more pronounced so that the CO-oxidation becomes faster and only one narrow peak (see fig. 1a) can be observed. The time of the first maximum is best predicted by the Leeds1.5 [2] mechanism whereas the simulated times of the Davis et al. [3] mechanism are about a factor of 2 too short. For the dilution 1:5, the first maximum at early reaction times predicted at the highest temperatures of this series could not be found in the experiments.

For the 50% $H_2 / 50\%$ CO mixture, the Davis et al. [3] mechanism shows a good agreement with the experiments only for temperatures lower than about 1075 K. For higher temperatures the simulated ignition delay times are up to a factor of 2 too short. The GRI3.0 [1] mechanism predicts up to a factor of 3 too long ignition delay times in the whole temperature range of the measurements. The model of Li et al. [4] agrees well with the measured values for the higher temperatures of this study. For lower temperatures it predicts ignition delay times up to a factor of 2 too long.



Fig. 2: Measured and simulated ignition delay times of 5% H_2 / 95% CO / O_2 / Ar (Φ =0.5) mixtures. Dashed lines indicate time of first OH*-maximum predicted.



Fig. 3: Measured and simulated ignition delay times of 50% H₂ / 50% CO / O₂ / Ar (Φ =0.5) mixtures.

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