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Brief Communications

The effects of CO addition on the autoignition of H_2, CH_4 and CH_4/H_2 fuels at high pressure in an RCM

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ABSTRACT

Autoignition delay times of stoichiometric and fuel-lean ($\varphi = 0.5$) H_2, H_2/CO, CH_4, CH_4/CO, CH_4/H_2 and $CH_4/CO/H_2$ mixtures have been measured in an Rapid Compression Machine at pressures ranging from 20 to 80 bar and in the temperature range 900–1100 K. The effects of CO addition on the ignition of H_2, to 50% CO in the fuel, and CH_4, to 20% CO in the fuel, are observed to be negligible both experimentally and computationally for the conditions studied here. The addition of syngas to methane results in ignition behavior that resembles an equivalent methane/hydrogen fuel mixture with the same hydrogen fraction. In contrast to results previous presented in the literature, we thus observe no inhibiting effect from CO for the conditions in our experiments.

1. Introduction

The drive to reduce the emissions of CO_2 and the desire to diversify the fuel supply have resulted in an increasing interest in the use of syngas and in the possible addition of syngas to natural gas as alternative fuels in combustion equipment. These mixtures of predominantly CO and H_2 are produced mainly from thermal gasification of biomass or coal. Understanding of the autoignition behavior of pure syngas and methane/syngas mixtures is an integral aspect of the development and benchmarking of chemical mechanisms of syngas and hydrocarbon fuels, and is essential to guarantee safe and efficient operation of current and future combustion equipment. Regarding operational aspects, changes in the autoignition delay time of the fuel can result in engine knock in internal combustion engines or pre-ignition in lean-burn premixed gas turbines. Both phenomena should be avoided since they can physically damage the equipment. Insight into the autoignition behavior of the fuel is also indispensable for development of Homogeneous Charge Compression Ignition engines. Central to the analysis of ignition behavior is data from well-defined experiments.

Several experimental studies of H_2/CO ignition have been conducted; most of which performed at pressures below 3 bar (e.g., [1–5]). To our knowledge, only a few experimental studies report autoignition delay time measurements of H_2/CO mixtures at conditions relevant for turbines and gas engines [5–10]. In Ref. [9] autoignition measurements of $H_2/CO/N_2/O_2/CO_2$ mixtures were performed in a Rapid Compression Machine (RCM) at pressures ranging from 7.1 to 26.4 atm, temperatures from 855 K to 1051 K, equivalence ratios from $\varphi = 0.1–1.0$ and H_2:CO ratios from 0.25:4.0. Whereas the data presented suggest a significant effect of the H_2:CO ratio (also observed in the analysis of the data in Ref. [11]), the authors conclude that the ignition delay times can be predicted by an expression independent of the H_2:CO ratio. The results reported in [7,8], presenting ignition delay times from RCM measurements at pressures ranging from 15 to 50 bar, temperatures from 950 K to 1100 K and equivalence ratios from 0.36 to 1.6, show that the addition of CO to H_2 increases the autoignition delay time. Moreover, the inhibiting effect of CO was seen to be more pronounced at higher pressures. Given the seemingly contradictory conclusions and the mechanistic discussion in the literature [11] regarding the influence of CO on the oxidation chemistry of H_2-mixtures at high pressures, it is interesting in this context to revisit the effect of CO on the ignition properties of hydrogen.

In light of the potential addition of significant quantities of biomass-derived syngas as a method for “greening” natural gas, it is also of interest to consider the effects of H_2/CO mixtures on the ignition properties of methane, as a model system. Such mixtures are also relevant when considering synthetic natural gas (SNG), in which substantial fractions of CO and H_2 have been catalytically

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Table 1
composition of $CH_4/H_2/CO$ mixtures (mole fractions).

φ	CH_4	H_2	CO	O_2	N_2	Ar	CH_4:H_2:CO
1	0.091	0	0	0.182	0.3	0.427	1:0:0
0.5	0.048	0	0	0.190	0.3	0.462	1:0:0
1	0	0.286	0	0.143	0.3	0.271	0:1:0
0.5	0	0.167	0	0.167	0.3	0.367	0:1:0
1	0	0.143	0.143	0.143	0.3	0.271	0:0.5:0.5
0.5	0	0.117	0.050	0.167	0.3	0.367	0:0.7:0.3
1	0.069	0.041	0.028	0.172	0.3	0.390	0.5:0.3:0.2
0.5	0.037	0.022	0.015	0.185	0.3	0.441	0.5:0.3:0.2
1	0.080	0.034	0	0.177	0.3	0.409	0.7:0.3:0
0.5	0.042	0.018	0	0.188	0.3	0.452	0.7:0.3:0
1	0.084	0	0.021	0.179	0.3	0.416	0.8:0:0.2

converted to methane [12]. While the reduction of the ignition delay time of methane by hydrogen addition at conditions relevant to engines and turbines seems well established ([13,14] and references therein), to our knowledge no autoignition measurements have been performed in $CH_4/CO/H_2$/oxidizer mixtures.

Here we report the autoignition delay times of stoichiometric and fuel-lean ($\varphi = 0.5$) H_2, H_2/CO, CH_4, CH_4/CO, CH_4/H_2 and $CH_4/CO/H_2$ mixtures using O_2/N_2/Ar oxidizers at pressures ranging from 20 to 80 bar and temperatures from 900 to 1100 K, measured in an RCM.

2. Experimental and simulation methods

The autoignition measurements reported in this study are performed in an RCM whose details are described elsewhere [15,16]. The composition of the H_2, H_2/CO, CH_4, CH_4/CO, CH_4/H_2 and CH_4/H_2/CO gas mixtures studied, expressed as mole fractions, are presented in Table 1. The gas compositions were chosen to investigate the autoignition behavior of common syngas compositions produced from hydrocarbons or biomass [12] and expected blends of natural gas with hydrogen, CO and syngas. All gas mixtures were manometrically prepared in advance in a 10-liter aluminum gas cylinder and allowed to mix for ~72 h. The gases used in the mixtures all have a purity greater than 99.99%. To avoid iron pentacarbonyl $Fe(CO)_5$ formation at high pressures [17], the presence of which can affect the autoignition delay time significantly [11,18] all CO-containing gases (the pure CO from the producer and the resulting fuel/air mixtures) were stored in aluminum cylinders. Mass spectrometric analyses of the fuel/air mixtures showed that the presence of iron-containing species in the samples was below the detection limit of 1 ppm. The N_2/Ar ratio is chosen to provide similar temperatures after compression for each fuel mixture. As mentioned above, the peak pressures P_c were varied between, 20 and 80 bar and the peak temperatures, T_c, in the range 900–1110 K by changing the initial pressure of the mixture and the compression ratio. The reproducibility of the measured autoignition delay time is ~5%, and the positioning reproducibility of the compression ratio yielded a variation in the temperature of ±2 K resulting in roughly 10% additional scatter in the data measured along the isotherms and isobars. Knowledge of the composition of the test mixtures, initial temperatures and pressures allowed us to calculate the temperature after compression assuming the existence of an adiabatic core [19].

The autoignition measurements are compared with numerical simulations using the SENKIN code [20] and a chemical mechanism [21–25][1] that includes the recommended rate expression for the reaction $CO + HO_2 = CO_2 + OH$ [26] intended to reconcile the effect of CO in H_2 mixtures on the measured ignition delay times at high pressures. The effects of heat loss and varying specific volume during the experiment is taken into account into the simulations and described in detail in [16]. Figure 1 shows a typical measured pressure trace[2], and the results from simulation of these conditions.

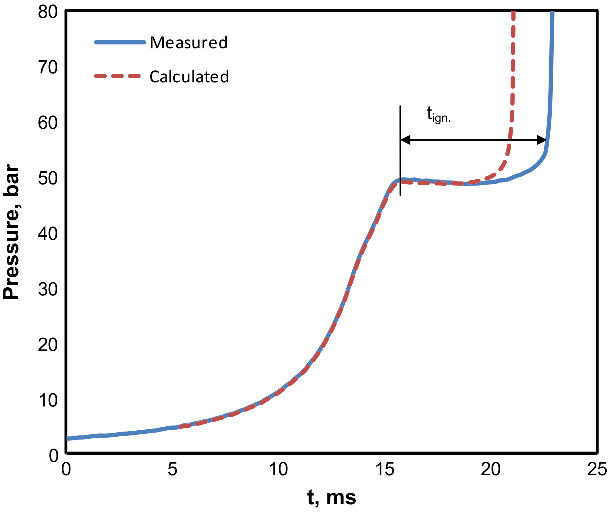

Fig. 1. Measured and modeled pressure traces for a fuel lean ($\varphi = 0.5$) $CH_4/H_2/CO/N_2$/Ar mixture at $T_c \sim 995$ K.

3. Results and discussion

The measured (points) and calculated (lines) autoignition delay times are presented in two sets; in the first set (Figs. 2 and 3) the ignition delay times are presented as function of temperature at constant pressure and in the second set (Fig. 4) the ignition delay times are presented as function of pressure at a fixed temperature (along an isotherm). Further, to facilitate comparison the solid points represent the measured ignition delay times in the fuels without CO, while the open symbols in the same color represent the same fuel with added CO. Since the measured delay times under stoichiometric conditions are substantially shorter than measured under fuel-lean conditions the measurements at constant pressure are shown at 40 bar for $\varphi = 1$ (Fig. 2) and at 50 bar for $\varphi = 0.5$ (Fig. 3) to provide a similar range of measured delay times.

As can be seen in Figs. 2–4, the measured ignition delay times for the binary mixtures of CO with hydrogen (up to 50% CO) and methane (up to 20% CO in the mixture) are indistinguishable from those of the pure fuels H_2 and CH_4, respectively. This observation is in contrast to the results reported in [7,8] where addition of CO to H_2 resulted in a substantial increase in the autoignition delay time, roughly a factor of 2 under similar experimental conditions. We note that the autoignition delay times of the pure H_2 mixtures, when scaled by the oxygen concentration, are in good agreement with those reported in Refs. [7,13,27]. The origin of this discrepancy for the CO/H_2 containing mixtures is at present unclear. Referring to the discussion surrounding Fig. 10 in Ref. [11] on the temperature dependence of hydrogen/syngas ignition, we also note that the data presented here, when scaled to the conditions used in that figure, follow the slower "branch" of the ignition data at lower temperatures. We observe in passing that, as concluded in Ref. [28], differences between the two branches are due to facility-specific differences in the experimental venue. As also recently shown [29] for H_2/O_2 mixtures, non-ideal behavior (observed as an increase in pressure) in shock tube data at lower temperatures/longer delay times tends to shorten the computed delay time, as compared to the ideal constant-volume assumption, while non-ideality in

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[1] The NUIG mechanism can be downloaded from http://c3.nuigalway.i.e./naturalgas3.html

[2] Note: the data are available upon request for simulations.

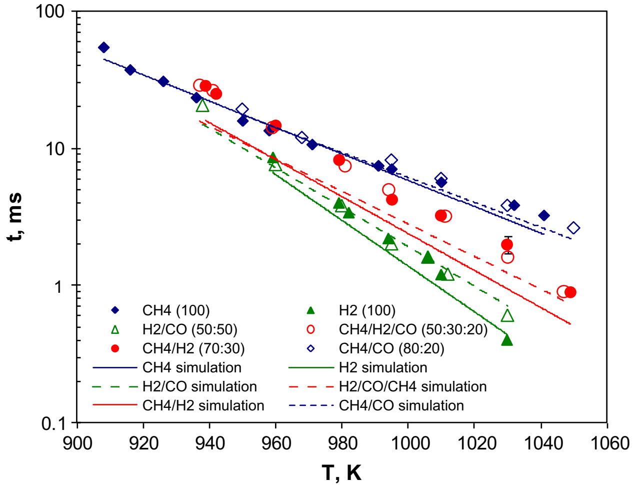

Fig. 2. Measured autoignition delay times of stoichiometric $CH_4/CO/H_2/O_2/N_2/Ar$ mixtures as function of temperature at a constant pressure, $P_c \sim 40$ bar.

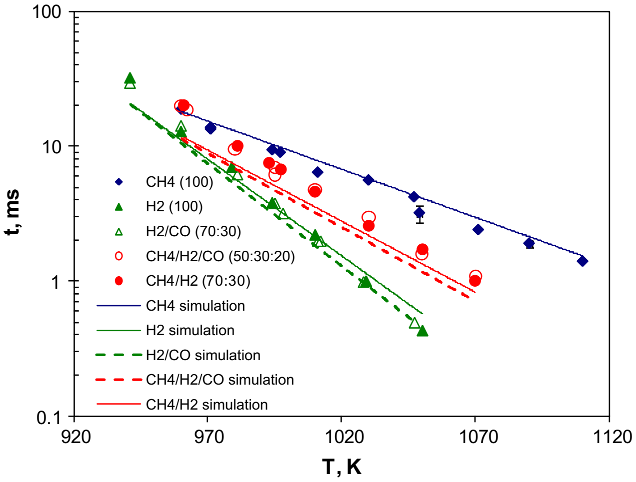

Fig. 3. Measured autoignition delay times of fuel lean ($\varphi = 0.5$) $CH_4/CO/H_2/O_2/N_2/Ar$ mixtures as function of temperature at a constant pressure, $P_c \sim 50$ bar.

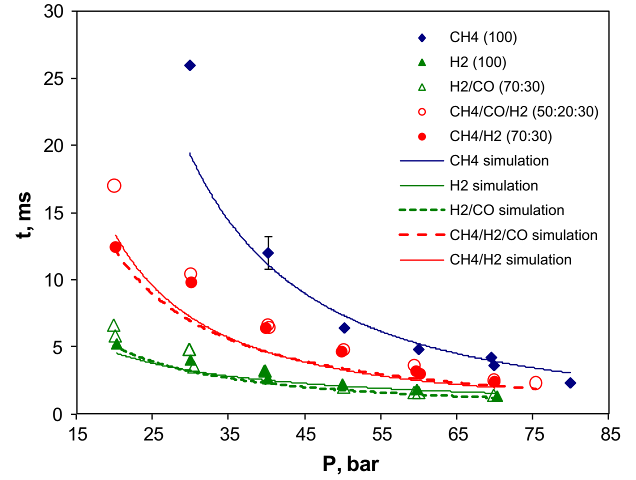

Fig. 4. Measured autoignition delay times of fuel lean ($\varphi = 0.5$) $CH_4/CO/H_2/O_2/N_2/Ar$ mixtures as function of pressure at a constant temperature, $T_c \sim 1010$ K.

RCM measurements (a decrease in pressure/temperature in the adiabatic core) tends to lengthen the delay times. This latter effect has been recognized as essential for modeling RCM data for several years ([19] e.g.), while the consideration of non-ideality in modeling shock tube data is relatively recent [30]. Thus, the respective non-idealities in the two experimental venues drive the determined ignition delay times systematically apart, and can easily reach factors of 5 or higher [11]. In light of this, it would seem that parameters, such as activation energy, that are derived directly from experimental data should be regarded with circumspection.

The experimental results show that addition of 30% H_2 in methane results in a substantial reduction in the autoignition delay time for both $\varphi = 1$ (Fig. 2) and $\varphi = 0.5$ (Figs. 3 and 4); moreover the ignition promoting effect of hydrogen in methane is more pronounced at higher temperatures, as also observed in [13,14] under similar conditions. Regarding CO addition to this mixture, the observation that the measured ignition delay times in the three component mixtures $CH_4/H_2/CO$ (50:30:20, equivalent to a 50% addition of a syngas with H_2/CO ratio of 60:40) is identical to the binary mixture CH_4/H_2 (70:30) for both equivalence ratios (see Figures) suggests that CO in the $CH_4/H_2/CO$ mixtures behaves similarly to CH_4. Given that the fractions of all species in the fuel–air mixture change upon “replacement” of 20% of the methane by CO in the fuel, caution should be exercised in generalizing this result. As an aside, the computations show a *decrease* (of only 25%) when varying the CO fraction in the fuel from 0% to 60% (CH_4 fraction ranges from 70% to 10% at constant 30% H_2 in the fuel).

Figures 2–4 show that with the exception of the stoichiometric CH_4/H_2 mixtures the measurements (points) and calculations (lines) are generally in good agreement, quantitatively varying between 5% and 40% depending upon the mixture. The largest difference between measurements and calculations for stoichiometric CH_4/H_2 mixtures is 70%, which deserves further examination. We also remark that the lines are best fits through the simulations of the individual conditions; the individual simulations follow the variation in the data better than the fit. Consistent with the experimental observations, no substantial difference in the calculated ignition delay time is observed between fuel mixtures with (solid lines) and without (dotted lines) CO. We note here that the current mechanism [21–25] predicts a significantly slower increase in the ignition delay time with increasing CO fraction in H_2; at 50 bar, $\varphi = 1$ and $T = 1000$ K the delay time doubles at ~90% CO, in contrast to the predictions of mechanisms used in [7,11], which were adjusted to match the experimentally observed inhibition of CO, and show a much more rapid rise, doubling at 50% CO. Taken together, these results suggest only a modest effect of CO addition to H_2, CH_4 and CH_4/H_2 fuels. Based on the current experimental and numerical results we suggest that the further experimental reexamination across a wider range of fuel composition is warranted.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.combustflame.2012.06.021.

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