

# Carbon monoxide detonations

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## Abstract

Carbon monoxide is of fundamental interest as a principal intermediate product in hydrocarbon combustion. The oxidation mechanism of CO has been extensively studied (Gardiner 1984), and researchers have found that in the presence of hydrogen-containing substances the oxidation is performed almost entirely by the hydroxyl molecule. However little data are available on the detonation characteristics of CO. The aim of the present study is to investigate the addition of different hydrocarbons to detonations of CO in air.  $H_2$ ,  $C_2H_2$ ,  $C_2H_4$ , and  $C_6H_{14}$  were chosen so as to study the effects of variations in atomic hydrogen content and chemical structure. Detonations were characterized by pressure, velocity and cell width measurements.

## Experimental Setup and Procedure

This study is conducted in a 7.3 m long, 280 mm internal diameter stainless steel detonation tube (Fig. 1). All gases are of chemically pure grade (99% purity). The detonation is initiated by an acetylene-oxygen driver mixture which is injected in the vicinity of an exploding wire just prior to initiation. The energy as determined by measurements of the driver gas is approximately 70 kJ. Three PCB pressure transducers record the pressure and time-of-arrival of the wave as it propagates through the tube. The equilibrium code STANJAN (Reynolds 1986) is used to calculate the Chapman-Jouguet wave speed, pressure, and temperature. The wave speed is derived from the time-of-arrival data is checked against that calculated by STANJAN, and is within  $\pm 1\%$ .

Cell width measurements are obtained by inserting a sooted foil into the downstream end of the tube. The shock triple points in the passing detonation scour a cellular pattern in the soot. Since the cellular structure for CO detonations is inherently quite irregular, about 10 cell width measurements are made from which a minimum, maximum, and average cell width are recorded for each foil. Cell width measurements also exhibit significant variations due to observer judgement and to the inherent nonuniformity of the three-dimensional detonation recorded on a two-dimensional surface.

## Results

Cell width measurements (Fig. 2) are given for varying volume fractions of  $H_2$ ,  $C_2H_2$ ,  $C_2H_4$  and  $C_6H_{14}$  in stoichiometric CO/Air at 100 kPa and 297 K, where 'Air' is  $O_2 + 3.76 N_2$ . Without the addition of any H-containing species, a detonation in stoichiometric CO/ $O_2$  could not be initiated with the initiation

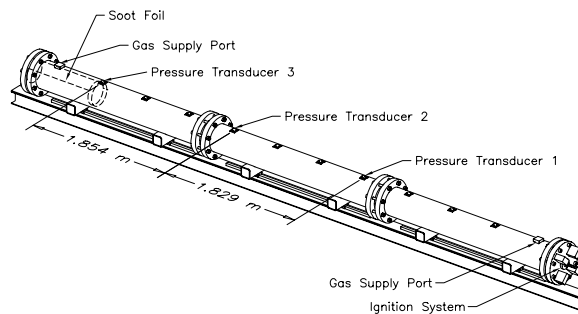


Figure 1: Gaseous detonation facility

system previously described, and only a decaying blast wave resulted. Increasing the fuel mole fraction,  $\alpha$ , of all four hydrocarbons decreases the measured cell width. By comparing the slopes of Fig. 2, it appears that  $H_2$  and  $C_2H_2$  are the most effective in reducing the cell width, followed by  $C_2H_4$ , and finally  $C_6H_{14}$ . Any conclusions drawn from comparing the limiting fraction of each hydrocarbon must be tentative as many more data points are required to achieve statistical significance. Nevertheless, by comparing the extrapolated cell widths for small fractions of hydrocarbon, it appears that for a particular value of  $\alpha$  the cell widths are smallest for addition of  $C_6H_{14}$  and largest for  $H_2$ .  $C_6H_{14}$  addition also produced a detonation at the lowest fuel fraction ( $\alpha = 0.0025$ ).

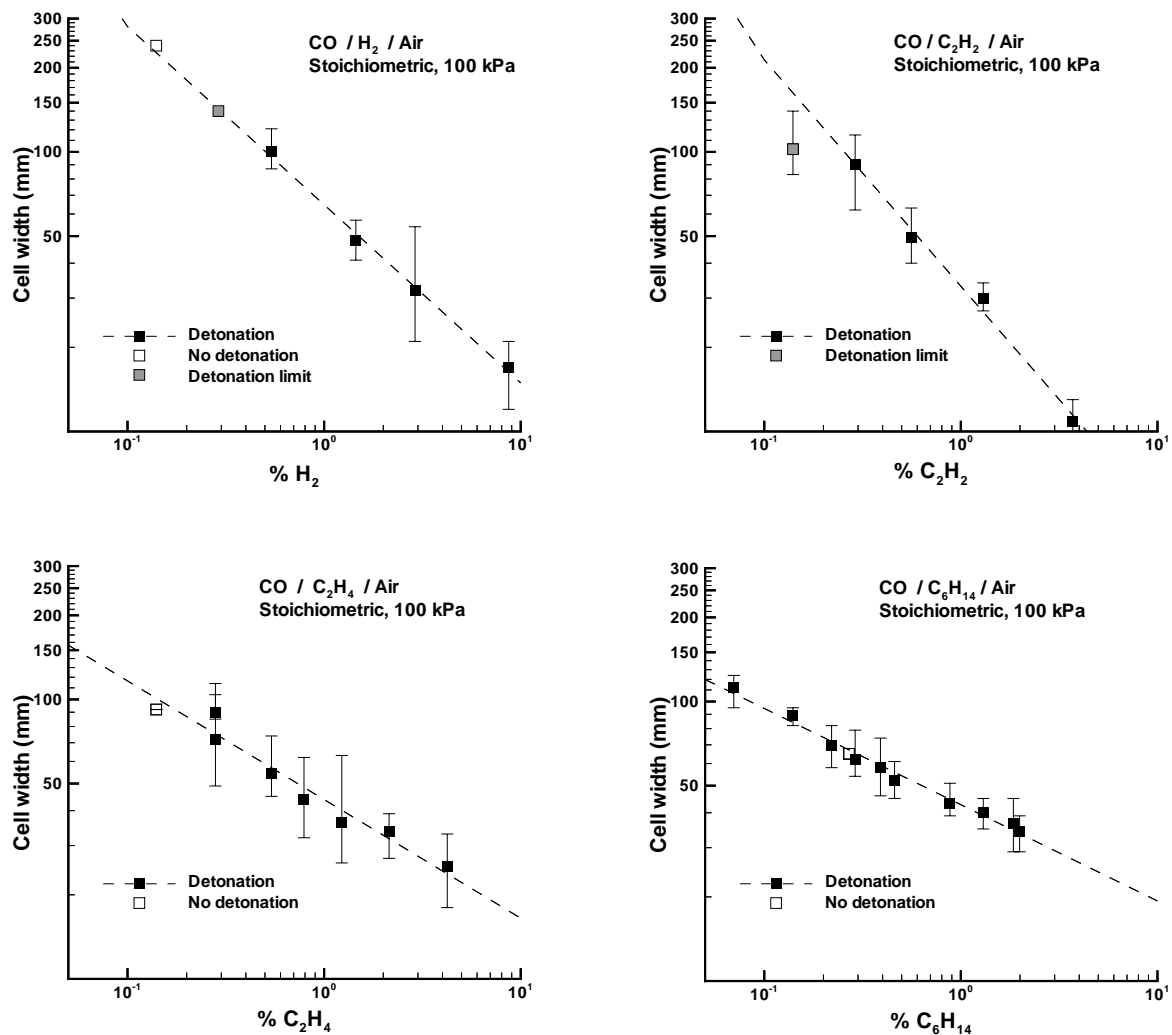


Figure 2: Cell widths measurements for CO/Hydrocarbon/Air. Curves are interpolated from the cell widths of successful detonations. Error bars represent minimum and maximum measured cell widths. The detonation limit denotes a value where both detonation and failure were observed.

In order to further understand these results, the chemical kinetics must be examined. Yetter et al.(1991) report a validated mechanism for CO/ $H_2$ / $O_2$  kinetics, but no mechanism is available that has been validated for both CO and higher molecular weight hydrocarbons. This is largely due to the lack of appropriate experimental data. Mechanisms that have been previously validated for both  $H_2$  and  $C_2H_4$  detonations are being used to obtain induction zone times from constant volume calculations for comparison with Yetter et al.'s CO/ $H_2$ / $O_2$  results and with shock tube data. Reaction zone lengths can then be calculated with a code (Shepherd 1986) which uses the one-dimensional Zel'dovich-von Neumann-Doring detonation model together with CHEMKIN II (Kee 1989) chemical kinetics subroutines. This process is continuing; some results are given in Fig. 3.

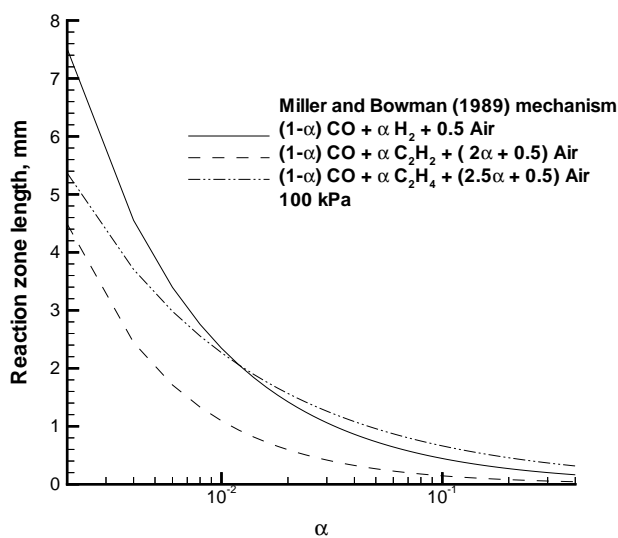
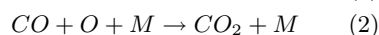


Figure 3: Reaction zone length calculations for varying fuel mole fraction,  $\alpha$ .

## Discussion

Cell widths were found to decrease with increasing fuel mole fraction of  $H_2$ ,  $C_2H_2$ ,  $C_2H_4$ ,  $C_6H_{14}$ , in order of effectiveness. As the critical energy required to initiate a spherical detonation is proportional to the cube of the cell width (Lee 1982), the mixture becomes more sensitive to detonation in all cases. This result are supported by previous studies which found triply-bonded  $C_2H_2$  to be more sensitive to detonation than doubly-bonded  $C_2H_4$ , which is itself more sensitive than an singly-bonded alkane like  $C_6H_{14}$  (Tieszen et al. 1991). Extrapolated data indicates  $C_6H_{14}$  produces the smallest cells and  $H_2$  the largest at low values of  $\alpha$ . A detonation was initiated for much lower mole fractions of  $C_6H_{14}$  (down to 0.07% of the total mixture) than for  $H_2$  (0.29% of total mixture).



In the presence of H-containing species, the oxidation of CO has been shown (Gardiner 1984, Yetter et al. 1991) to be performed almost entirely by reaction (1) rather than by (2). In a numerical study of  $H_2/CO/Air$  flames at 100 kPa, Warnatz (1979) found that (2) becomes important only at low values of  $H_2$  mole fraction, accounting for 40% of  $CO_2$  produced when the mole fraction of  $H_2$  is less than 0.1%. Although oxidation kinetics are influenced by transport processes in flames (Yetter et al. 1986), the present results agree with Warnatz in that if reaction (2) becomes increasingly dominant at low H concentrations, the kinetics will inhibit detonation initiation and be insufficient to sustain a detonation. Results indicate that at lower values of  $\alpha$ ,  $C_6H_{14}$  can decompose to produce enough H atoms so that sufficient oxidation occurs by (1) to sustain the detonation. For  $H_2$  mixtures at low  $\alpha$ , the kinetics become dominated by reaction (2) and the detonation fails. This indicates that an important criterion for determining the detonation limits for CO/hydrocarbon mixtures is the H atom concentration present in the induction zone. Validated chemical kinetics mechanisms are being sought to model the relevant concentrations through the reaction zone. This study is also being extended to include other hydrocarbons and give further consideration to the molecular structure of the H-containing species.

## References

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