Influence of the initial temperature on the detonability of CH4/H2/O2/N2 mixtures

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Introduction

In order to reduce the output of gas responsible for the greenhouse effect (carbon-dioxide) from hydrocarbons combustion, the industrial community tends to use methane, or even mixtures of methane with hydrogen. Then, for safety concerns, the problem of detonability of such mixtures becomes of primary importance, as well as the more general problem of detonability of reactive mixtures made of two fuels and used in a lot of chemical processes.

Characteristics of the reactive mixtures such as critical point source initiation energy Ec or critical diameter dc of detonation transmission are representative of their detonability. These characteristics are the expression of a critical curvature for the existence of the self-sustained detonation. The corresponding radius Rc is proportional to the cell size λ of the steady self-sustained detonation. The values of Ec and dc are then directly correlated to this cell size λ by the relations $Ec \sim \lambda^3$ and $dc \sim \lambda$ [1].

Hydrogen is a very detonable fuel when mixed with air while methane is the less detonable among the most common fuels. In fact, at ambient temperature and pressure in stoichiometric proportion with air, their detonation cell sizes are respectively $\lambda_{H2} \sim 1cm$ and $\lambda_{CH4} \sim 30cm$. The main goal of this work is to improve the knowledge of the parameters controlling the detonability of the reactive mixtures made of these two fuels of very different detonability.

Experimental conditions

The molar formulation of the studied mixtures is given by the expression:

$$x H_2 + (1-x)CH_4 + (2-1.5x)(O_2 + \beta N_2)$$
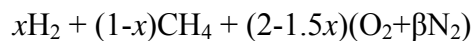
where x varies from 0 to 1 and $\beta = N_2/O_2$ from 0 (oxygen) to 3.76 (air).

We have studied the steady self-sustained detonation:
- of each fuel (x=0 or 1),
- and of mixtures made of the two fuels defined here over,
with respect to the initial pressure P_0 (0.1 to 2bars), initial temperature T_0 (293K and 473K) and nitrogen dilution β ($0 \leq \beta \leq 3.76$) [2].

We used an experimental device that allows carrying the gaseous mixtures to high initial temperatures (close to their auto-ignition limits) in a few minutes. The detonation tube (7m long and 52mm internal diameter) is supplied with a direct current of 1500A and indeed, heated by Joule effect [3].

We characterized the detonation of these mixtures by measuring:
- their local detonation velocity all along the tube by a non intrusive method using a Doppler hyperfrequency interferometer,
- their characteristic cell structure width λ by the soot tracks technique.

Results

Analysis of our results shows that, whatever the initial temperature and nitrogen dilution:
- the measured velocities of steady self-sustained detonations are very close to the CJ ones (within 1%), except for spinning detonations,
- the evolution of the cell size λ of the steady self-sustained detonation of the mixtures with respect to the initial pressure is very similar to that already determined for mixtures made of a single fuel, i.e.:

$$\lambda \sim P_0^{-n}$$

with $1.1 \leq n \leq 1.2$.

The values of λ deduced from these data at P_0=1bar, for T_0=293 and 473K are plotted versus x on Fig. 1.
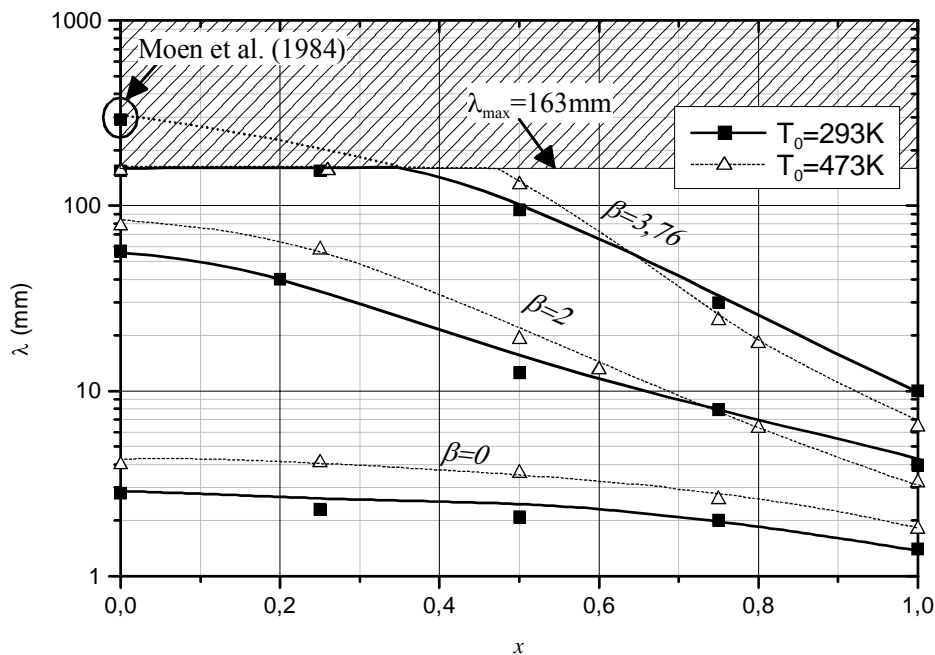

Figure 1. Mean cell size λ of the detonation of the mixtures xH$_2$ + (1-x)CH$_4$ + (2-1.5x)(O$_2$+βN$_2$) versus x for three values of β (0 ; 2 and 3.76) at P_0=1bar and T_0=293 et 473K.

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The hatched zone above λ=163mm (see Fig. 1) is not allowed in our experimental conditions since the maximum value of the detonation cell width that can be measured in an experimental tube of internal diameter d is λ_{max}=πd (spinning detonation). It means that for β=3.76 and $x \leq$0.4-0.5 the values of the measured cell size are not representative of the real values of λ.

We can analyze each set of curves separately:

1. For β=0 and $0 \leq x \leq 0.75$, replacement of CH_4 by H_2 in the mixture at given T_0 modifies very weakly the value of λ.
On the whole range of x ($0 \leq x \leq 1$), λ increases with T_0 (293K to 473K) by about 40%. Therefore, the detonability drops when the initial temperature increases. This trend had already been shown with single fuel based mixtures ($C_2H_4/O_2/Ar$ [3], C_2H_2/O_2 [4], H_2/O_2 [5]).

2. For β=2, the influence of T_0 on λ is very different from the previous case. For x=1 (H_2 + $0.5(O_2+\beta N_2)$) an increase of T_0 leads to a decrease of λ and the reverse for x=0 (CH_4 + $2(O_2+\beta N_2)$). The inversion occurs at x~0.75 .

3. For β=3.76, the useful range of x is limited to $0.5 \leq x \leq 1$. For x<0.5 the mean cell size is invariant. In order to allow an interpolation between x=0 and 0.5 for T_0=293K, we have reported on Fig.1 the value λ=280mm obtained by Moen et al [6] for the stoichiometric mixture (CH_4-Air). The effect of T_0 on the mixtures with a very high proportion of H_2 is stronger in comparison to the case β=2. The decrease of λ (consequence of the increase of T_0) is very clear in this case and the inversion point moves towards x~0.65.

Conclusions

Unlike a widespread idea according to which a mixture CH_4-O_2-N_2 would be strongly sensitized by the addition of a small proportion of H_2, our results show that the replacement of 20% in moles of CH_4 by H_2 in the CH_4-O_2-N_2 mixture has nearly no effect on the mean cell size of its detonation and therefore on its detonability.

This prevailing effect of the heavier fuel on the detonability of a gaseous mixture containing two fuels had already been observed by measurements of critical initiation energy of (C_2H_6-CH_4) mixtures (Bull et al, 1979, [7]).

The influence of the initial temperature on the detonability of the studied mixtures depends on the nitrogen dilution. The detonability of the non diluted ones (β=0) decreases when the initial temperature increases. For β=2 and 3.76 this trend reverses respectively for x>0.75 and x>0.65.

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