

Critical Tube Diameter in a Two Reaction-Steps Detonation:

H₂/NO₂ mixture

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1 Introduction

The critical diameter d_c of detonation transmission from a tube of i.d. d to free space represents one of the main criteria characterising the detonation sensitivity of a reactive mixture [1, 2, 3].

For usual fuels mixed with oxygen and slightly diluted with nitrogen (or with other two or three-atomic diluent), d_c is correlated to the detonation cell width λ_{c1} by a quasi universal constant $k_c = 13$ (i.e. $d_c = 13\lambda_{c1}$ [4]). Nevertheless, recent results obtained with hydrogen and some common fuel mixed with air show that $d_c/\lambda \sim 18-24$ [5,6].

Large discrepancies in the value of k_c have been observed also in mixtures highly diluted by a monatomic gas [7, 8]. In particular, dilution of stoichiometric H₂/O₂ and C_nH_m/O₂ mixtures by argon, helium or krypton up to 50% in volume has nearly no influence on k_c (=13) while dilution up to 75-80% doubles its value[8].

Many different geometrical diffraction conditions from a tube to free space (or to half-space) have been studied in the past (various shapes of normal diffraction section, central obstacles of different shapes and blocage ratios). In all these experimental conditions, k_c can differ from 13 but remains constant for a given geometrical condition demonstrating the self-similarity to the cell width of the detonation diffraction phenomenon. An exception appears also with systems highly diluted by Argon when self-sustained detonation diffracts from a cylindrical tube to diverging cones of various angles [9].

These conclusions are only valid for the above-mentioned reactive systems where the oxidizer is oxygen. Their detonation exhibits only a single cellular structure. Below they will be referred as “one reaction-step” mixtures in a global sense.

On the contrary, recent studies on mixtures where the oxidizer NO₂ is mixed with H₂ or with hydrocarbon (CH₄, C₂H₆) or included in the chemical formula of a monopropellant as nitro or nitrate group [10], clearly show that the chemical energy is released here in two main successive exothermic steps inside the detonation reaction zone. These steps are characterized:

- for stoichiometric and rich mixtures by two local maxima of reaction rates of very different characteristic times τ_{i1} and τ_{i2} or lengths Li_1 and Li_2 ($Li_2/Li_1 > 10$, [10,11]) each time being defined as the delay between the leading shock wave and each maximum of reaction rate. We have shown that the two exothermic steps of chemical induction lengths Li_1 and Li_2 are correlated to the two nets of cellular structure of characteristic size λ_1 and λ_2 (λ_1 nested in λ_2).

- for lean mixtures, by only one maximum of reaction rate corresponding to the first step of characteristic time τ_{i1} (and length Li_1), and by a single cellular structure of size λ_1 . Even in these conditions the chemical energy release is also non-monotonous.

So, being interested to determine the dynamical behaviour of these detonations and in particular their critical conditions of existence, we carried out an experimental study of the detonation diffraction in H₂/NO₂ mixture from a cylindrical tube to half space. For this mixture at ambient initial temperature and for different pressures, we know the ranges of equivalence ratio ϕ for which the detonation cellular structure is unique or double and the corresponding cell sizes. The goal of this study was to determine the critical diameter relationship for detonations with non-monotonous energy release.

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2 Experimental

We have studied the critical tube diameter in H_2/NO_2 mixtures in the range of equivalence ratio $0.4 < \phi < 1.3$, at the initial temperature $T_0 = 293K$ and initial pressures $0.3 < p_0 < 1.25$ bar.

The experimental set up consists of a stainless steel tube of 52 mm i.d. and 7 m length. One end was connected to a coaxial chamber of 200 mm i.d. and 500 mm length. Mixtures were prepared directly inside the tube and the chamber, using partial pressures method taking into account the chemical equilibrium between NO_2 and N_2O_4 . Mixtures homogenisation was insured by a recirculation pump. Detonation was initiated directly at the closed end of the tube by an exploding wire or by a high explosive charge. Self-sustained detonation pressure, velocity and cell size were systematically measured just before the plane of diffraction. Detonation diffraction was recorded using smoke-foil technique.

3 Results and Analysis

For each equivalence ratio ϕ , we have decreased the initial pressure down to the critical pressure $p_0 = p_{0c}$ for which the detonation transmission fails. For all the experiments, detonation velocities were close to their C J values within 1%.

We have reported in Fig 1 the critical initial pressure p_{0c} with respect to ϕ . The U-shape curve shows a minimum for $\phi = 0.6-0.7$. This result is not surprising since the detonability of H_2 -based mixture is higher for lean mixtures.

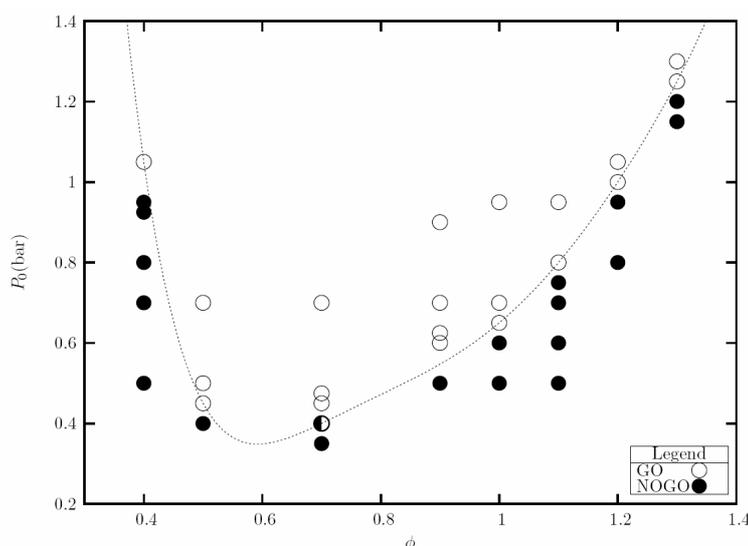


Fig 1 : Critical initial pressure p_{0c} for detonation transmission versus equivalence ratio ϕ , in H_2/NO_2 mixtures at $T_0=293$ K. Black circle: "no Go"; Open circle: "Go"

The mean features of detonation diffraction were analysed from smoke-foils (cf Fig 2). Results show that detonation diffraction differs from that observed in one reaction-step detonation (i.e. with monotonous heat release). Indeed, in the case of critical transmission of one reaction-step detonation, the head of the lateral expansion fan destroys instantaneously the detonation cells outside of the unperturbed central diffraction cone. Detonation re-initiates after the shock-reaction zone decoupling in the vicinity of the axis at a distance of about $1.5-2d$ from the tube exit. A transverse detonation propagates in the narrow zone of pressurised reactive mixture between the leading shock and combustion products and re-initiates the detonation of the whole charge. In the two-step detonation studied here, cells associated to the first step enlarge when submitted to the expansion fan before being destroyed progressively while the larger ones, when they exist, disappear immediately. Thus, the second reaction step vanishes and is probably not efficient for the detonation re-initiation. Detonation reinitiates like in one-reaction step systems. However, during the diffraction, the lateral propagation of the decaying shock

wave depends on ϕ . At $\phi=0.5$, diffraction (Fig 2a) looks like the one-reaction step diffraction while in rich mixture ($\phi=1.1$, Fig 2b) the lateral propagation of the decaying leading shock wave is very limited due to a fast and important loss of energy sustaining the shock propagation.

Knowing the variation of the sizes of the two cellular structures (i.e. λ_1 et λ_2) and the single one (λ_1) with respect to the equivalence ratio (cf [11]), for each $p_{0c}(\phi)$ we have established the relationship $d_c = k \lambda$.

The value of k is defined for the fine cell over the entire range of equivalence ratio ($k = k_1$) and for the larger cell ($k = k_2$) only for $\phi > 1$. Variations of k_1 and k_2 values in function of ϕ are reported in Fig 3. We notice that:

- 1°) k_1 is an increasing function of ϕ , from 17-18 for $\phi = 0.5$ to 45-50 for $\phi = 1$ and up to 100 for $\phi = 1.3$,
- 2°) k_2 remains approximately constant and equal to 3-4.

These values are far from the classical value $d_c/\lambda=13$ relative to C_nH_m/O_2 and H_2/O_2 mixtures presenting practically only one reaction step. Nevertheless, one can notice that, as ϕ decreases, k_1 becomes closer to 13.

The studied mixtures exhibit two main exothermic global reactions ($A \rightarrow B$ and $B \rightarrow C$) which lead for stoichiometric and rich mixtures to a double cellular structure whereas for lean mixtures only to a single one.

- the first global reaction ($A \rightarrow B$) called reaction (1) is written for $\phi > 0.5$ as:



- the second global reaction ($B \rightarrow C$) called reaction (2), is written as:

for $\phi < 1$:



for $\phi > 1$:



The reaction (1) is relative to the oxidation of a part of H_2 by O_2 , the reaction (2) to the oxidation of H_2 by NO . These two oxidizers are provided by the NO_2 decomposition and their oxidation characteristic times are very different [11].

Figure 4 displays the total heat of reaction $Q = Q(1)+Q(2)$ ($Q(1)$ and $Q(2)$ being heat of reactions (1) and (2) respectively) in function of ϕ and the ratio $Q(1)/Q$. One can notice that this ratio is maximum at 67% for $\phi = 0.5$ and decreases to 36% at $\phi = 1$. This value remains constant for $\phi > 1$.

Some specific comments about the critical diffraction of two reaction-step detonation are the following:

1°) for stoichiometric and rich mixtures exhibiting two nets of cells of very different sizes (at least of one order of magnitude), the number of cells needed for transmission in a diameter is 3-4 if we consider the larger cell representative of the reaction (2). This diffraction appears markedly promoted if compared to that of reactive mixtures with O_2 as oxidizer for which $d_c/\lambda=13$. The main reason lies in the existence of the reaction (1) of the very short characteristic time providing 36% of the total energy. This reaction is significantly less sensitive to the drastic expansion effects during the detonation diffraction.

Let us consider now the critical detonation transmission results based on finer cells. Their number needed in a tube diameter is 50 to 100 depending on ϕ . In that case, these cells are representative of the smaller part (36%) of the total energy, while 64% being released with a very long characteristic time increasing with ϕ . Thus, the reaction (2) ceases to support detonation during the sudden expansion and does not take part to the detonation re-initiation in the near field flow. So, the critical finer cell number must be greater than 13.

During the critical diffraction of the double cellular detonation, re-initiation of detonation is then controlled mainly by the finer cellular structure, the few larger cells present in the tube diameter disappear during the drastic expansion. These larger cells appear again in the case of successful detonation transmission but far from the tube exit where the radius of curvature of the detonation is large.

2°) for detonation diffraction of lean mixtures exhibiting only a single cellular structure representative of the sole reaction (1), the number of cells in the tube diameter decreases when the contribution of this reaction to the total energy release increases, i.e. when ϕ decreases. For $\phi = 0.5$, k_1 becomes "closer" to the classical value of 13 of a one reaction-step detonation. Indeed, in that case, the second part of the energy release destroyed during the diffraction process, as explained above, represents only 33% of the total energy. One can think that if the energy of the delayed step (reaction (2)) becomes small compared with the first one, then k should evolve toward 13.

Finally one can notice that $d_c/\lambda = 26-30$ for $\phi = 0.8$. This value corresponds also to that of stoichiometric C_2H_2/O_2 mixture diluted by 80% of Argon.

4 Conclusion

Conditions of critical detonation diffraction from a tube to free space in mixtures obeying a non-monotonous two reaction-step energy release (i.e. a fast first step $A \rightarrow B$ of short delay followed by a slow second step $B \rightarrow C$) have been determined experimentally. The mixture used is H_2/NO_2 exhibiting single or double cellular structure depending on the non-monotonous energy release law varying with the equivalence ratio ϕ .

When the quasi-CJ detonation is a one-cell detonation, corresponding to lean mixtures, d_c/λ_1 varies from 17-18 ($\phi=0.5$) to 50 ($\phi \sim 1$) that is significantly larger than 13 of the classical law. For detonation with a double cellular structure, d_c/λ_1 increases from 50 ($\phi \sim 1$) to 100 ($\phi=1.3$) while d_c/λ_2 is quasi constant and equal to 3-4. One can underline that the larger is d_c/λ_1 relative to 13, the larger is the contribution of the second step to the total energy release.

Besides, in a completely different chemical system, it has been shown that a second reaction step appears when the dilution by a monatomic gas of a fuel-oxygen mixture becomes large. We have shown that this non-monotonous heat release is at the origin of the large d_c/λ observed [9].

So, in a more general way, detonation in gaseous systems can be thought to proceed according to two main above mentioned exothermic reaction steps. The first step would be responsible of the cellular structure, the second being at the origin of larger cells provided that a characteristic time of this step can be associated with the existence of a local maximum of the reaction rate. The increase of d_c/λ above 13 is attributed to the increase of the relative contribution of the second exothermic step to the total chemical energy.

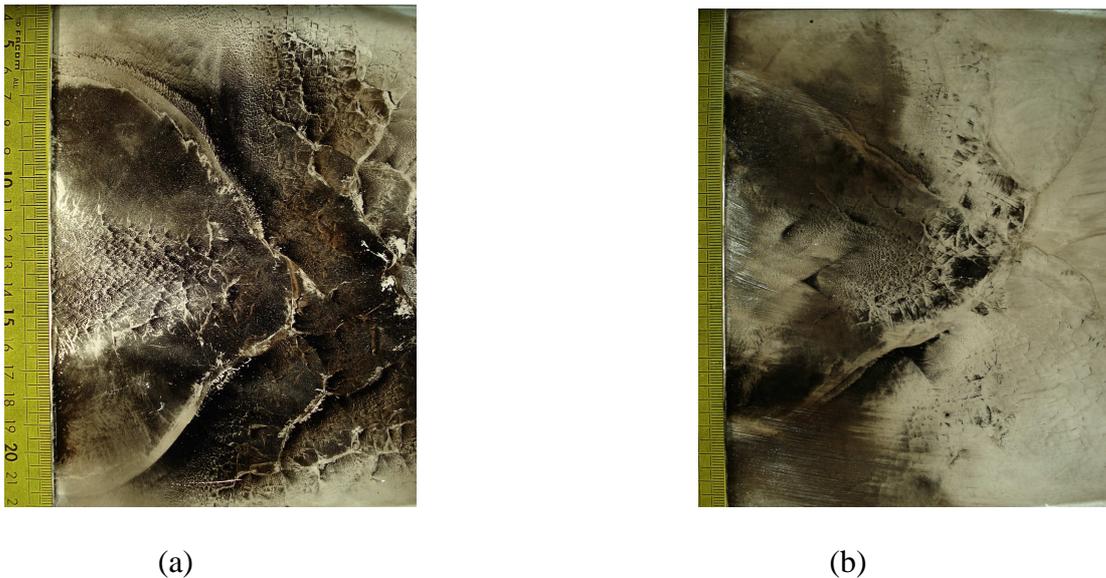


Fig 2 : Examples of smoke foil records of detonation diffraction in H_2/NO_2 mixture :
(a) one-cell detonation: $\phi = 0.5$, $p_0 = 0.5$ bar; (b) two-cells detonation: $\phi = 1.1$, $p_0 = 0.95$ bar

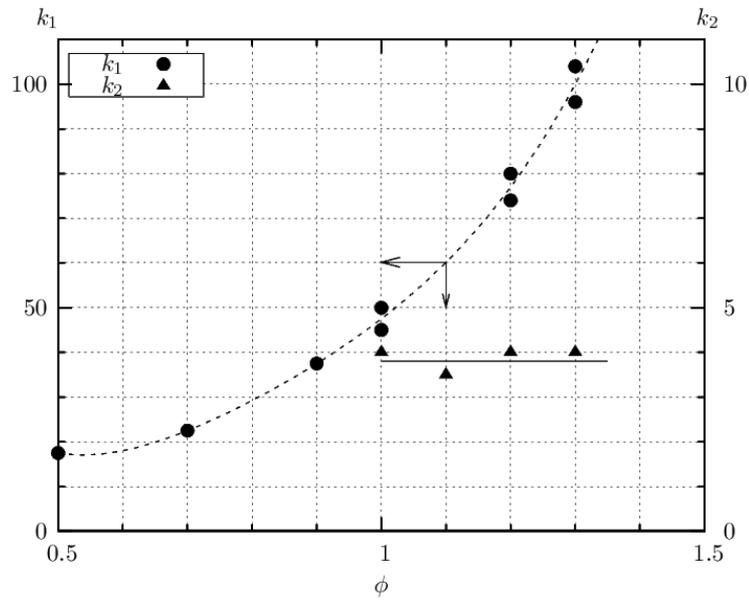


Fig3: Variation of k_1 and k_2 versus equivalence ratio ϕ .

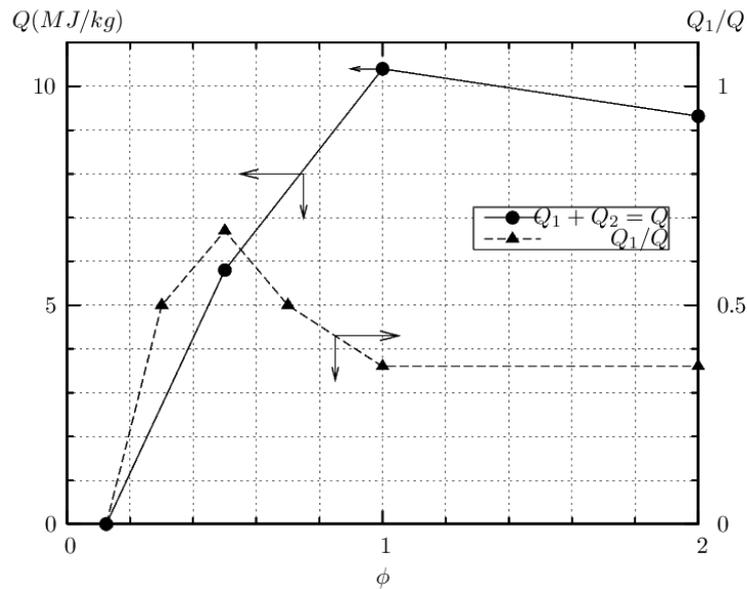


Fig 4 :Variation of $Q=Q_1+Q_2$ and Q_1/Q versus equivalence ratio ϕ .

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