

# The initiation of methane/air autoignition: the important chemical components for various initial conditions

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## Introduction

Reactive systems introduce a wide range of time scales, the fastest of which (i) are of *dissipative* character and (ii) tend to constrain the evolution of the system on a low-dimensional surface in phase space; i.e., on the *slow invariant manifold (SIM)*. On this surface, the system is characterized by slower time scales that lead the system to equilibrium or away from it. The case where some of these slow time scales are of *explosive* character [1,2] (i.e., the components of the system that generate them tend to lead the system away from equilibrium) will be considered here. The *CSP* algorithmic tools [1-6] will be employed, in order to (i) investigate the explosive modes that develop at the initiation of the autoignition process for various initial temperatures and pressures and (ii) identify the species that relate to the explosive time scales and the reactions that are responsible for the generation of these time scales.

## The Computational Singular Perturbation method

Consider a system consisting of  $N$  ordinary differential equations (ODE's):

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) = \frac{\mathbf{W}}{\rho} \left( \mathbf{S}_1 R^1(\mathbf{y}) + \dots + \mathbf{S}_K R^K(\mathbf{y}) \right) \quad (1)$$

where  $\mathbf{y}$  is the  $N$ -dim. vector of the species' mass fractions,  $\rho$  is the mixture density,  $\mathbf{W}$  is a  $N \times N$  diagonal matrix with the species' molecular weights in the diagonal,  $\mathbf{S}_k$  is the  $N$ -dim. stoichiometric vector of the  $k$ -th reaction and  $R^k(\mathbf{y})$  is the corresponding reaction rate. Eq.(1) can be cast in *CSP* form as:

$$\frac{d\mathbf{y}}{dt} = \sum_{n=1}^N \mathbf{a}_n f^n, \quad f^n = \mathbf{b}^n \cdot \mathbf{g}(\mathbf{z}) = \sum_{k=1}^K \left( \mathbf{b}^n \cdot \frac{\mathbf{W}}{\rho} \mathbf{S}_k \right) R^k \quad (2)$$

where  $\mathbf{a}_n$  is the  $N$ -dim. *CSP* basis vector of the  $n$ -th mode,  $\mathbf{b}^i \cdot \mathbf{a}_j = \delta_j^i$  and  $f^n$  is the related amplitude [5,6]. Assuming that the system in Eq. (2) exhibits  $M < N$  time scales that are of dissipative nature and much faster than the rest ( $\tau_1 < \dots < \tau_M \ll \tau_{M+1} < \dots < \tau_N$ ), yields:

$$f^m \approx 0 \quad (m = 1, M) \quad \frac{dz}{dt} \approx \sum_{n=M+1}^N \mathbf{a}_n f^n \quad (3)$$

The first relation defines the SIM, while the second governs the slow evolution of the process on the SIM. The decomposition in fast/slow processes of the vector field  $\mathbf{g}(\mathbf{y})$  allows the acquisition of significant physical understanding of complex chemical systems and it is possible by the use of *CSP*-related algorithmic tools:

$$J_k^n = \frac{c_k^n}{|c_1^n| + \dots + |c_N^n|} \quad P_k^n = \frac{\mathbf{b}^n \cdot \mathbf{W} \mathbf{S}_k R^k}{|\mathbf{b}^n \cdot \mathbf{W} \mathbf{S}_1 R^1| + \dots + |\mathbf{b}^n \cdot \mathbf{W} \mathbf{S}_K R^K|} \quad D_i^n = a_i^n b_i^n \quad (4)$$

where,  $c_k^n = \mathbf{b}^n \cdot \text{grad}(\mathbf{S}_k R^k) \cdot \mathbf{a}_n$  and, by definition,  $\sum_{k=1}^K |J_k^n| = \sum_{k=1}^K |P_k^n| = \sum_{i=1}^N a_i^n b_i^n = 1$  [1-3]. *Time Scale Participation Index*,  $J_k^n$ , measures the relative contribution of the  $k$ -th reaction to the  $n$ -th eigenvalue  $\lambda_n$  (therefore, to the time scale  $\tau_n$ ), while *Amplitude Participation Index*,  $P_k^n$ , measures the relative contribution of the rate of the  $k$ -th reaction to the amplitude of the  $n$ -th *CSP* mode  $f^n$ . Finally, *CSP Pointer*,  $D_i^n$ , measures the relation of the  $n$ -th mode to the  $i$ -th component of  $\mathbf{y}$ .

## The Physical Problem

The homogeneous adiabatic autoignition at constant volume of a homogeneous stoichiometric  $\text{CH}_4/\text{air}$  mixture is considered. The chemical kinetics mechanism employed here was derived from the GRI 3.0 mechanism after ignoring the nitrogen chemistry reactions.

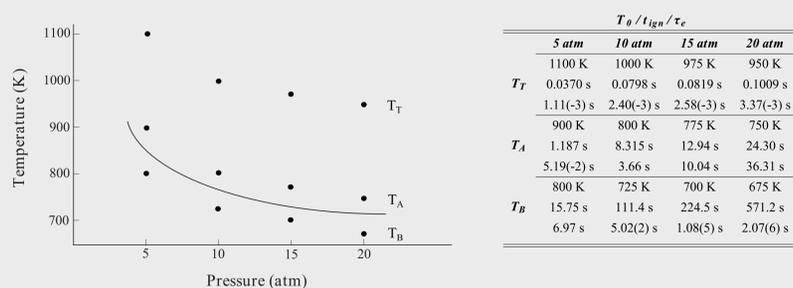


Fig. 1: Left: Explosion limit of methane/air [7,8]. Right: Values of  $T_0$  and  $p_0$ , along with the related ignition delay times  $t_{ign}$  and the fastest explosive time scale  $\tau_e$  at  $t = 0$ .

The  $t=0$  case will be considered only. The purpose of this investigation is to examine the initiation of the process, by considering various initial pressures and temperatures. Here, four different values of the initial pressure  $p_0$  will be examined, while three different values for the initial temperature  $T_0$  will be accounted for each  $p_0$ . The slow dynamics of the system considered here exhibits two explosive time scales. Only the fastest one, say  $\tau_e$ , will be considered, since this is the one that characterizes the autoignition process.

## Analysis of the fast explosive mode

In all cases considered, the reaction contributing the most towards the temperature evolution is reaction  $\text{HO}_2 + \text{CH}_3 \leftarrow \text{O}_2 + \text{CH}_4$  (118b), followed in a distance by reaction  $\text{H} + \text{CH}_3(+M) \leftarrow \text{CH}_4(+M)$  52b. API data show that at  $t = 0$  the amplitude  $f^e$  of the fast exhausted mode is entirely due to reaction (118b), in all cases considered.

|       |                        | Pointer |        |        |        |
|-------|------------------------|---------|--------|--------|--------|
|       |                        | 5 atm   | 10 atm | 15 atm | 20 atm |
| $T_T$ | $\text{CH}_3$          | +0.74   | +0.65  | +0.61  | +0.56  |
|       | $\text{HO}_2$          | +0.14   | +0.17  | +0.17  | +0.17  |
| $T_A$ | $\text{CH}_3$          | +0.35   | +0.90  | +0.92  | +0.93  |
|       | $\text{CH}_2\text{O}$  | +0.31   | +0.08  | +0.07  | +0.06  |
| $T_B$ | $\text{CH}_2\text{O}$  | +0.92   | +0.96  | +0.95  | +0.98  |
|       | $\text{H}_2\text{O}_2$ | +0.07   | +0.03  |        |        |

Table 1: Species, the mass fractions of which are identified by the *CSP Pointer*.

According to Table 1, when  $T_0 > 900\text{K}$  the variable that relates the most to the fast explosive time scale is the  $\text{CH}_3$  radical, followed by the  $\text{HO}_2$  radical. This finding is in full agreement with the TPI data, which identify reaction  $\text{CH}_3 + \text{O}_2 \rightarrow \text{O} + \text{CH}_3\text{O}$  (155f) as the one contributing the most to  $\tau_e$ , followed by reactions  $2\text{CH}_3(+M) \rightarrow \text{C}_2\text{H}_6(+M)$  (158f) and  $\text{CH}_3 + \text{H}_2\text{O}_2 \leftarrow \text{HO}_2 + \text{CH}_4$  (157b). Clearly, the identified variables are reactants of the reactions that generate  $\tau_e$ . When  $900\text{K} > T_0 > 700\text{K}$ , Table 1 shows that the *CSP Pointer* identifies  $\text{CH}_2\text{O}$  as the one related the most to  $\tau_e$ . TPI data show that reactions (158f),  $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{HO}_2 + \text{HCO}$  (32f) and  $\text{CH}_3 + \text{O}_2 \rightarrow \text{OH} + \text{CH}_2\text{O}$  (156f) are the ones contributing the most to  $\tau_e$ . In the two cases where  $T_0 < 700\text{K}$ , Table 1 indicates that the variable associated the most with  $\tau_e$  is the temperature  $T$ . TPI data show that the reactions contributing the most to  $\tau_e$  are (158f), (156f) and (118b). The presence of the *O-H* chemistry has a negligible influence here.

From the results displayed in Table 1 we can conclude that the fast exhausted time scale  $\tau_e$  at  $t = 0$  is mainly determined by the rate of oxidation of (i)  $\text{CH}_3$  when  $T_0$  is high and of (ii)  $\text{CH}_2\text{O}$  when  $T_0$  is low. At very low temperatures the variable that relates to the explosive mode is the temperature. The effect of pressure does not seem to be that much important in determining the nature of the initiation of the autoignition process.

## Conclusions

Algorithmic asymptotic analysis was employed in order to identify the species and the reactions in which they participate as reactants that relate the most to the explosive time scale that characterizes an autoignition process. A homogeneous  $\text{CH}_4/\text{air}$  mixture was considered at various initial temperatures and pressures.

Although in all cases considered reaction  $\text{HO}_2 + \text{CH}_3 \leftarrow \text{O}_2 + \text{CH}_4$  (118b) was shown responsible for initiating the process, its reactants ( $\text{CH}_4$  and  $\text{O}_2$ ) were not shown to relate to  $\tau_e$  at  $t = 0$ . Instead, the reactants (e.g.,  $\text{CH}_3$ ,  $\text{CH}_2\text{O}$ ,  $\text{HO}_2$ ) of reactions that become active later on in the process were shown to relate at this starting point.

The predominant role of mainly  $\text{CH}_3$  and  $\text{CH}_2\text{O}$  and secondary of  $\text{HO}_2$  at high and low, respectively, initial temperatures is well documented in the existing literature regarding the action of the various reactions after the initiation of the process [7,8]. Here it was shown that the consumption of these intermediate species relate the most to  $\tau_e$  at  $t = 0$ , although the rates of the consuming reactions there are practically zero, since the mass fraction of at least one of the reactants are zero at  $t = 0$ . In addition, it was shown that at very low temperatures,  $\tau_e$  is mostly related to  $T$ .

The fact that the  $\text{CH}_3$ ,  $\text{CH}_2\text{O}$  and  $\text{HO}_2$  consuming reactions (155f), (156f), (158f), (32f) and (157b) determine  $\tau_e$  at  $t = 0$  does not contradict the fact that their rates is zero there because the mass fraction of these species is zero [3]. Keeping in mind that  $\tau_e$  measures the time frame in which the autoignition takes place, these findings suggest that,  $\tau_e$  is mainly dependent to the mass fraction in the initial mixture of the other reactants ( $\text{O}_2$  for (155f), (156f) and (32f),  $M$  for (158f) and  $\text{CH}_4$  for (157b)). In other words, the magnitude of  $\tau_e$  is determined by the initial concentrations of  $\text{O}_2$ ,  $M$  and  $\text{CH}_4$  to the extend the reactions (155f), (156f), (158f), (32f) and (157b) consume  $\text{CH}_3$ ,  $\text{CH}_2\text{O}$  and  $\text{HO}_2$ .

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