Two Stage Ignition of *n*-heptane: Identifying the Chemistry Setting the Explosive Time Scales

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Abstract— The explosive time scales developing during a two stage ignition of n-heptane are examined. The elementary reactions contributing the most for their development are identified.

I. INTRODUCTION

In reacting systems, a wide spectrum of time scales arise, rendering the mathematical model stiff. Usually, the fastest time scales are of *dissipative* character, forcing the solution to evolve on a low dimensional manifold. However, some of the intermediate time scales are of *explosive* character and relate directly to ignition. From the early works on reacting systems based on time scale analysis, it was well understood that interesting information, such as ignition delays and chain-branching mechanisms, can readily be derived by analyzing these explosive modes [1].

Recent work has revealed that these explosive time scales need not be present in a flame configuration, where diffusion is the main mechanism for initiating the reaction process in the fresh mixture [2]. In contrast, in homogeneous systems the absence of transport makes the development of such kind of time scales a necessity for ignition.

The algorithmic methodology of Computational Singular Perturbation (CSP) method [1], [3] was employed for the identification of the chemical kinetics components responsible for the amplitudes of the explosive modes developing during a two-stage ignition of *n*-heptane and dimethyl ether [4], [5].

Here, the chemical kinetics components responsible for the developing explosive time scales during a two-stage ignition of *n*-heptane will be examined. The concept of *Time Scale Importance Index* will be employed, being a component of the CSP methodology, which has been successfully employed for the analysis of the time scales relating to the NO_x chemistry [6] and to the circadian cycle in the cell [7].

II. GOVERNING EQUATIONS AND METHODOLOGY

We consider homogeneous adiabatic ignition at constant volume of a stoichiometric *n*-heptane/air mixture at initial pressure of 13.5 bar and temperature of 850K, as in Ref. [4]. We employ a kinetic model consisting of N = 561 species and K = 2539 reactions [8], the forward and backward directions of which are considered separately. The governing equations for the species mass fraction and temperature are:

$$\frac{d\mathbf{y}}{dt} = \frac{1}{\rho} \mathbf{W} \left(\mathbf{S}_1 R^1 + \ldots + \mathbf{S}_{2K} R^{2K} \right)$$
(1)

$$\frac{dT}{dt} = \frac{1}{\rho c_v} \left(-\dot{H}_c + RT \sum_{i=0}^N \dot{\omega}_i \right) \tag{2}$$

where y is the N-dim. vector of the species mass fraction, ρ is the mixture density, W is a $N \times N$ matrix with the species molecular weights in the diagonal, \mathbf{S}_k and R^k are the N-dim. stoichiometric vector and rate of the k-th reaction, T is temperature, c_v is the heat capacity, \dot{H}_c is the heat release rate, R is the universal gas constant and $\dot{\omega}_i$ is the molar production rate of the i-th species.

These equations can be cast in the form of an (N+1) -dim. system:

$$\frac{d\mathbf{z}}{dt} = \mathbf{g}(\mathbf{z}) = \hat{\mathbf{S}}_1 R^1 + \ldots + \hat{\mathbf{S}}_{2K} R^{2K}$$
(3)

where z is composed of y and T and each additive term on the RHS corresponds to the forward or backward direction of the K reactions.

To leading order, the CSP vectors \mathbf{a}_i and covectors \mathbf{b}^i (i = 1, N), which define the directions in the phase space along which the i-th time scale act, can be approximated by the right and left, respectively, eigenvectors of the Jacobian J of g. In this case, the following expression for the developing time scales in the problem can be obtained:

$$\tau_i = |\lambda_i|^{-1} \tag{4}$$

where λ_i (i = 1, N) are the eigenvalues of **J**:

$$\lambda_i = \mathbf{b}^i \mathbf{J} \mathbf{a}_i \tag{5}$$

Given the decomposition of the RHS in Eq. (3), the i - th eigenvalue can be expressed as:

$$\lambda_i = \mathbf{b}^i \mathbf{Q}^1 \mathbf{a}_i + \dots + \mathbf{b}^i \mathbf{Q}^{2K} \mathbf{a}_i \tag{6}$$

where

$$\mathbf{Q}^{k} = grad\left(\hat{\mathbf{S}}_{k}R^{k}\right) \tag{7}$$

so that the contribution to the value of λ_i of the two directions of each of the K reactions can be computed.

In order to assess the contribution of each chemical reaction to the value of the *i*-th time scale τ_i , through

the related term in Eq. (6), the following *Time Scale Importance Index* is introduced:

$$J_k^i = \frac{\mathbf{b}^i \mathbf{Q}^k \mathbf{a}_i}{|\mathbf{b}^i \mathbf{Q}^1 \mathbf{a}_i| + \dots + |\mathbf{b}^i \mathbf{Q}^{2K} \mathbf{a}_i|}$$
(8)

where $\sum_{k=1}^{2K} |J_k^i| = 1$ [6]. J_k^i measures the contribution of the k - th reaction to the i - th time scale.

Explosive time scales relate to positive eigenvalues (or positive real parts, in case of a complex conjugate pair). Therefore, non-negligible positive values of J_k^i identify reactions having a significant influence in establishing the explosive character of the i - th mode and in making the corresponding time scale τ_i faster. However, the fact that λ_i is positive, does not preclude the possibility that some of the 2K additive terms in the RHS of Eq. (6) are nonnegligible and negative. In this case, the related reactions exhibit a significant influence to counter the explosive character of the i - th mode and make τ_i slower.

III. DYNAMICS OF TWO STAGE IGNITION

Shown in Figs. 1 and 2 are the evolution of temperature, fuel and representative final products; the two stages clearly depicted.



Fig. 1. The evolution of Temperature and mass fraction of n-heptane with time.



Fig. 2. The evolution of the mass fraction of co and oh with time.

The developing real positive eigenvalues (or real positive parts of complex eigenvalues), which according to Eq. (4) produce the explosive time scales, are displayed in Fig. 3.

It is shown that before the two temperature jumps there exist two explosive time scales, one fast and one slow; converging to each other at the start of each jump. As Fig. 4 clearly shows, in both cases the convergence of the two time scales follows their merging, as they become quickly slower on their way to loose their explosive character.

Next, Importance Indices for the explosive time scales before the two jumps will be presented, in order to clarify the operating explosive mechanisms in each temperature jump.



Fig. 3. The evolution of real positive eigenvalues (solid line) and real positive parts of complex eigenvalue pairs (broken line).



Fig. 4. Top: Magnification of the two temperature jumps. Bottom: the corresponding evolution of the real positive eigenvalues (solid line) and real positive parts of complex eigenvalue pairs (broken line).

IV. CHEMISTRY RELATED TO THE EXPLOSIVE TIMESCALES

Figure 5 shows the Importance Indices for the fast and the slow timescales at two instances, right before the first stage of ignition. In this period, the top row of Fig. 5 shows that the fast time scale is mainly set by isomerization reactions of RO_2 to QOOH (R denotes $C_n H_{2n+1}$ and Q denotes $C_n H_{2n}$ groups) as well as of peroxyalkylhydroperoxides $(QOOH - O_2)$ to ketohyperoxides and OH, in agreement with Ref. [4]. This latter step is particularly significant both because it initiates the preparation of the OH pool, which will be very significant for the dynamics at later times, see Fig. 2, but also because the decomposition of ketohyperoxides can lead to low-temperature chain-branching [8]. As shown in the bottom row of Fig. 5, the time scale of the slow chemistry in this period is mainly carried first $(t = 0.3704 \times 10^{-3} s)$ by termination reactions, such as $ho2 + ho2 \rightarrow h2o2 + o2$ or by reactions generating OH such as $c714ooh2 - 4o2 \rightarrow c714ooh2 - 4 + o2$ followed by the decomposition $c714ooh2 - 4 \rightarrow c7h14o2 - 4 + oh$. Later on $(t = 0.4664 \times 10^{-3} s)$ the contribution of $c714ooh2-4o2 \rightarrow c714ooh2-4+o2$ and of c714ooh3-



Fig. 5. Importance Indices right before the first jump. Top row: the fast time scale. Bottom row: the slow time scale. Left column: $t = 0.3704 \times 10^{-3} s$ ($\lambda_{fast} = 0.2657 \times 10^{5} s^{-1}$, $\lambda_{slow} = 0.9938 \times 10^{2} s^{-1}$). Right column: $t = 0.4664 \times 10^{-3} s$ ($\lambda_{fast} = 0.2421 \times 10^{5} s^{-1}$, $\lambda_{slow} = 0.3937 \times 10^{4} s^{-1}$).

 $5 \rightarrow c714ooh3 - 5 + o2$ to the slow timescale of the explosive mode is still important, but the importance of HO2 termination is diminished and can also occur through the alternate route $ho2 + oh \rightarrow h2o + o2$. It is worth noting that, as the two eigenvalues converge short before the first stage of ignition, the isomerization and oxygen addition reactions that promote strongly the fast-time-scale chemistry have an equally strong inhibiting effect on the slow chemistry.

Similarly, Fig. 6 shows the Importance Indices for the fast and the slow timescales at two instances right before the second stage of ignition. In this period, fast chemistry is carried out by chain-branching producing OH radicals (e.g. $h + o2 \rightarrow o + oh$ and $h2o2 + m \rightarrow oh + oh + m$) assisted first ($t = 0.2570 \times 10^{-2}s$) by low-C-number chemistry (mainly C2 and C1) and then ($t = 0.2584 \times 10^{-2}s$) by the strongly exothermic oxidation of CO. Similarly to what happens in the first stage, as the fast and

the slow eigenvalue approach to each other the reaction having the strongest positive contribution to the fast time scale (e.g. $h + o2 \rightarrow oh + o$) inhibits the slow time scale equally strong. Similarly, the reaction $o + oh \rightarrow h + o2$ seems to have a converse but equivalent effect, i.e. it inhibits the fast scale but promotes the slow one. Notably, the strongly exothermal $co+oh \rightarrow co2+h$ promotes both fast and slow chemistry.

V. CONCLUSIONS

For initial conditions that are of relevance to practical devices, the stoichiometric n-heptane mixture presents a two-stage ignition behavior. Both ignition stages occur at instances where two positive, real eigenvalues (corresponding to a fast and to a slow time scale) converge and yield one complex eigenvalue with a positive - but rapidly decreasing - real part. In both stages of ignition, the reaction groups contributing the most to the converging fast and slow time scales contain a significant number of



Fig. 6. Importance Indices right before the second jump. Top row: the fast time scale. Bottom row: the slow time scale. Left column: $t = 0.2570 \times 10^{-2} s$ ($\lambda_{fast} = 0.8253 \times 10^5 s^{-1}$, $\lambda_{slow} = 0.3003 \times 10^2 s^{-1}$). Right column: $t = 0.2584 \times 10^{-2} s$ ($\lambda_{fast} = 0.5778 \times 10^7 s^{-1}$, $\lambda_{slow} = 0.4705 \times 10^5 s^{-1}$).

reactions that have opposite effects to the fast and the slow chemistry, most usually favoring the fast and inhibiting the slow time scale.

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