

A Computational Analysis of Autoignition of H₂/Air Mixture with Temperature Fluctuations Using Computational Singular Perturbation

Wonsik Song¹, Efstathios-Al. Tingas¹, Su-Ryong Lee², Hong G. Im¹

¹ Clean Combustion Research Center, King Abdullah University of Science and Technology (KAUST)

Thuwal 23955-6900, Saudi Arabia

² Department of Automotive Engineering, Seoul National University of Technology
Seoul, South Korea

1 Introduction

Ignition of fuel-air mixtures is an important issue in modern engine applications, such as homogeneous charge compression ignition (HCCI) or low-temperature combustion (LTC) engines, towards higher efficiency and lower emissions. These engines operate in compression ignition (CI) mode with early fuel injection, such that the overall combustion phasing behavior is mainly dictated by the autoignition of nearly uniform fuel-air mixture. The mixture composition and temperature distribution is not perfectly uniform, however, due to the incomplete fuel-air mixing, wall heat losses, and the presence of residual gases. Therefore, the first occurrence of autoignition is usually localized, and such ignition “kernels” [1] grow into the development of subsequent autoignition or flame propagation in neighboring mixtures. From a Lagrangian standpoint, the evolution of chemical activities within the ignition kernel may be described as a reactive mixture pocket subjected to temporal fluctuations in temperature and composition during the induction period, where the timescales of the fluctuations depend on the level of turbulence and initial stratifications. For this reason, the response of the igniting mixture in the presence of imposed oscillations in temperature and fuel composition has been studied in the past [2,3]. For example, Bansal et al. [2] showed that a harmonic oscillation of temperature can lead to a net advancement or retardation of autoignition of the mixture depending on the frequency and phasing of the oscillation. As an extension of these fundamental studies, the present work employs the computational singular perturbation (CSP) tools in order to provide a more detailed analysis of chemical pathways responsible for the autoignition of homogeneous mixture in the presence of temperature fluctuations.

2 The mathematical model and CSP tools

The constant pressure autoignition of a homogeneous hydrogen/air mixture is governed by the species and energy equations (Eq. 1):

Correspondence to: stathis.tingas@kaust.edu.sa, hong.im@kaust.edu.sa

$$\frac{d\mathbf{y}}{dt} = \frac{1}{\rho} \mathbf{W} \cdot \sum_{k=1}^{2K} \mathbf{S}_k R^k \quad \frac{dT}{dt} = \frac{1}{\rho c_p} (-\mathbf{h}_c \cdot \mathbf{W}) \cdot \sum_{k=1}^{2K} \mathbf{S}_k R^k \quad (1)$$

where \mathbf{y} is the N -dimensional vector of the species mass fractions, \mathbf{S}_k and R^k represent the stoichiometric coefficients vector and reaction rate, respectively, of the k -th unidirectional reactions, ρ is the mixture density, \mathbf{W} is a $N \times N$ diagonal matrix with the species molecular weights in the diagonal, c_p is the specific heat under constant pressure, \mathbf{h}_c is the N -dimensional vector of the species absolute enthalpies, T is the temperature, and K is the total number of the reversible reactions. The chemical kinetics mechanism employed has been validated in a wide range of conditions [4].

The energy equation can be modified by accounting for an additional term as follows:

$$T_I(t) = T_0(1 + A \sin(2\pi ft)) \quad (2)$$

where T_0 is the initial temperature of the mixture, A and f are the amplitude and frequency of the oscillation, respectively, and t represents time. In that case, the energy equation in the Eqs. (1) is modified to the following Eq. 3:

$$\frac{dT}{dt} = \frac{1}{\rho c_p} (-\mathbf{h}_c \cdot \mathbf{W}) \cdot \sum_{k=1}^{2K} \mathbf{S}_k R^k + 2\pi f T_0 A \cos(2\pi ft) \quad (3)$$

The analysis of the dynamics of a stiff system requires the availability of a reduced model. CSP has been efficiently used for stiff systems and its tools have been proven to provide useful insight into the physical processes that relate to the evolution of the system [5-7]. According to CSP, Eqs. (1) can be cast in the form of the $(N+1)$ -dimensional system:

$$\frac{d\mathbf{z}}{dt} = \sum_{k=1}^{2K} \hat{\mathbf{S}}_k R^k = \sum_{n=1}^{N-E+1} \mathbf{a}_n f^n = \mathbf{g}(\mathbf{z}) \quad (4)$$

where $\mathbf{z} = [\mathbf{y}, T]^T$ is the $(N+1)$ -dimensional state column vector including the mass fractions and temperature, \mathbf{a}_n is the $(N+1)$ -dimensional CSP column basis vector of the n -th mode, f^n is the related amplitude defined by $f^n = \mathbf{b}^n \cdot \mathbf{g}(\mathbf{z})$, where \mathbf{b}^i is the $(N+1)$ -dimensional row i -th dual basis vector; thus $\mathbf{b}^i \cdot \mathbf{a}_j = \delta_j^i$ [8,9].

The timescale of each mode can be expressed by the relation $\tau_n = |\lambda_n|^{-1}$ ($n=1, \dots, N-E+1$), where λ_n is the n -th non-zero eigenvalue of the Jacobian \mathbf{J} of $\mathbf{g}(\mathbf{z})$. Considering that each eigenvalue is defined as $\lambda_n = \beta^n \cdot \mathbf{J} \cdot \alpha_n$ where α_n and β^n are the n -th right (column) and left (row) eigenvectors of the Jacobian \mathbf{J} of the system, respectively, then, each one can be expressed as:

$$\lambda_n = \beta^n \cdot \sum_{k=1}^{2K} \text{grad}(\hat{\mathbf{S}}_k R^k) \cdot \alpha_n = C_1^n + \dots + C_{2K}^n \quad (5)$$

since $\mathbf{J} = \text{grad}(\hat{\mathbf{S}}_1 R^1) + \dots + \text{grad}(\hat{\mathbf{S}}_{2K} R^{2K})$ [5]. C_k^n measures the contribution of the k -th reaction to λ_n and, therefore, to τ_n . A positive (negative) C_k^n implies that the k -th reaction favors (opposes) the explosive (dissipative) character of the n -th timescale τ_n [9].

3 Analysis of the hydrogen autoignition dynamics

In all calculations shown below, the initial conditions that were used were $T(0) = 1000$ K, $P(0) = 10$ atm, and $\phi(0) = 0.6$. To investigate the response of the ignition delay to the temporal fluctuations of the temperature, we computed the ignition delay time with increasing the frequency in Eq. 3, for several values of the amplitude. As can be seen in Fig. 1(a), the ignition delay time exhibits a harmonic oscillating

Table 1 The reactions providing significant contribution to the generation of the fast explosive timescale during the constant pressure autoignition of the H₂/air mixture.

Reaction number	Reaction	Reaction number	Reaction
1	H+O ₂ ⇌O+OH	12	HO ₂ +H⇌OH+OH
2	O+H ₂ ⇌H+OH	16/17	HO ₂ +HO ₂ ⇌H ₂ O ₂ +O ₂
3	OH+H ₂ ⇌H+H ₂ O	18	H ₂ O ₂ (+M)⇌2OH(+M)
9	H+O ₂ (+M)⇌HO ₂ (+M)	21	H ₂ O ₂ +H⇌H ₂ +HO ₂

response as a function of frequency, asymptotically tending to a value lower than the case where no fluctuation was imposed (for brevity this case will be referred to as reference case). Fig. 1(a) also shows that the asymptotic value of the ignition delay time becomes smaller as the amplitude increases. Additionally, regardless of the amplitude, once a frequency is applied to the system, the ignition delay time is always shorter than the reference case, implying that the temperature fluctuation always favors the ignition delay time of the hydrogen-air mixture.

To investigate the origin of the decrease of the ignition delay time, we chose an amplitude and frequency as 0.015 and 2520 Hz, respectively. The frequency is considered high enough such that it sufficiently approximates the asymptotic limit. Fig. 1(b) shows the temporal evolution of the temperature (black lines) and mass fraction of hydrogen (red lines) for the reference (solid lines) and fluctuating temperature (dashed lines) cases. The blue-dotted lines indicate the mean values of the fluctuating temperature condition. The figure shows that for the first and largest part of the process, the mean temperature value (blue dotted line) is the same as the temperature in the reference case (black solid line), while at the end it becomes larger than the reference case. On the other hand, the mass fraction of H is always larger in the fluctuating temperature case compared to the reference case. In order to investigate these findings further, tools generated in the framework of CSP were used.

4 Diagnostics

Fig. 2(a) shows all the timescales involved in the ignition process of the reference case where ten modes characterize the dynamic of the system. All of them have dissipative nature (black solid lines) except for two modes that are of the explosive nature (red dashed lines). One of the two explosive modes is the fast mode that is present throughout the so-called explosive stage [5], and the slow mode that

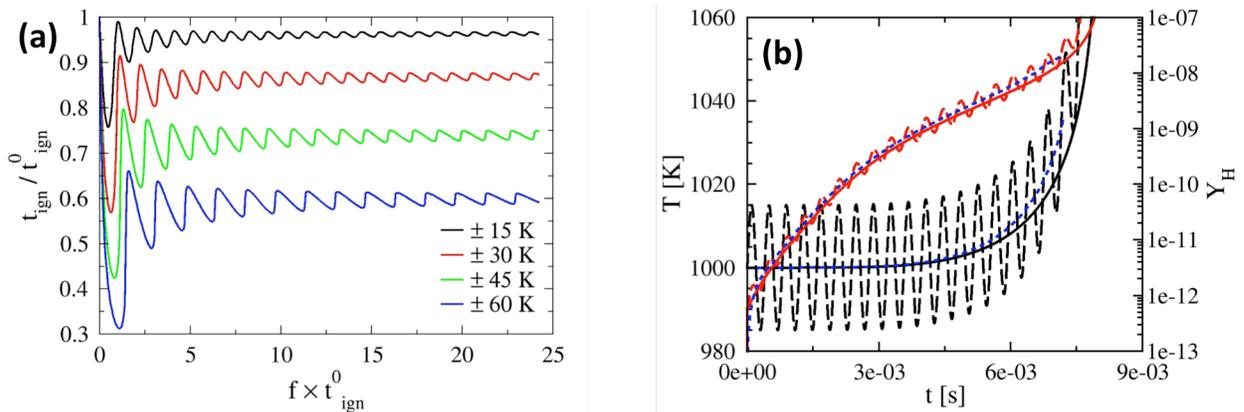


Fig. 1 Ignition delay time in response to the fluctuating temperature at different amplitudes (a) and temporal evolution of the temperature and the mass fraction of H during the autoignition process (b). Black and red lines indicate the temperature and the mass fraction of H, respectively, and solid and dashed lines are reference and fluctuating temperature case, respectively. Blue-dotted lines are the mean value of the fluctuating quantities.

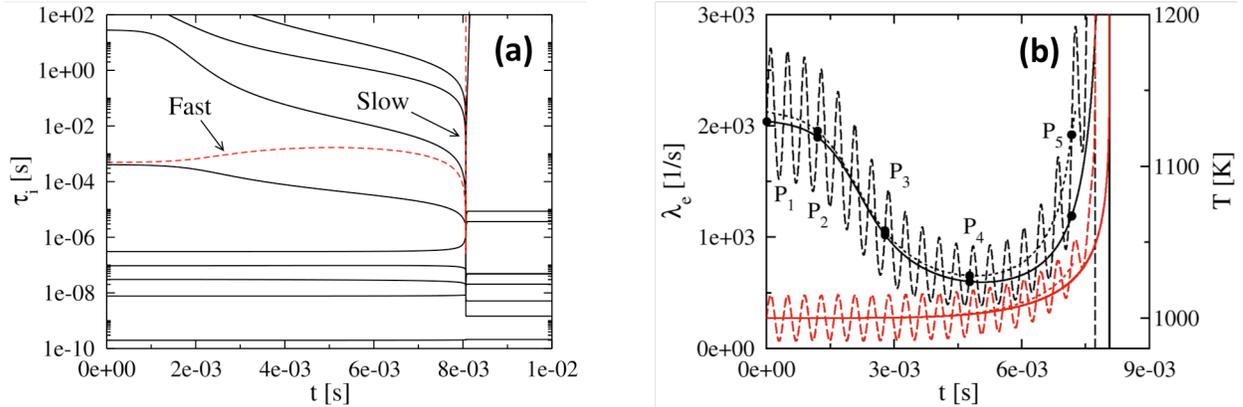


Fig. 2 Temporal evolution of all timescales involved in the present hydrogen-air system for the referent case (a) and explosive eigenvalue together with the temperature (b). For (b), Solid lines are the reference case and dashed lines are the fluctuating temperature case, and the dotted lines are the mean value of the oscillating case.

emerges at the very last part of the process, meets the fast one and then both disappear, implying the ignition happens. Fig. 2(a) also shows that a timescale gap is generated, indicating that the tangent space can be decomposed into fast and slow components and that the fast explosive timescale is on the top of this gap. Consequently, the fast explosive timescale is the characteristic timescale that drives the system away from equilibrium towards ignition. Fig. 2(b) displays the evolution of the fast explosive eigenvalue in both the reference and the fluctuating temperature cases. It is shown that the mean value of the fast explosive eigenvalue in the fluctuating temperature case is always larger than that in the reference case, therefore, explaining the shorter ignition delay time of the fluctuating temperature case. To identify the reactions that cause the larger value of the mean explosive eigenvalue, the CSP diagnostics C_s (Eq. 5), i.e., the contribution of each reaction to the explosive eigenvalue of the system, were calculated at five representative points and compared to those of the reference case. The results are summarized in Table 2, and Table 1 includes the descriptions of the reactions that appear in Table 2. It is noted that the selected points have been determined on locations where the fluctuating quantity crosses its mean one so that it can

Table 2 CSP diagnostics C_s for the reference case (upper) and the fluctuating temperature case (bottom) at the points indicated in Fig. 3.

	P1	P2	P3	P4	P5					
t [s]	0.000E+00	1.198E-03	2.786E-03	4.770E-03	7.174E-03					
λ_e [1/s]	2.042E+03	1.899E+03	1.021E+03	6.011E+02	1.190E+03					
T	1000.0	1000.0	1000.2	1002.5	1024.6					
Ref	21b	1.356E+03	21b	1.311E+03	21b	7.707E+02	18f	5.288E+02	1f	1.199E+03
	1f	7.549E+02	1f	7.476E+02	18f	7.399E+02	1f	5.132E+02	9f	-9.695E+02
	9f	-7.541E+02	9f	-7.467E+02	1f	6.141E+02	9f	-4.787E+02	18f	9.222E+02
	18f	6.829E+02	18f	7.207E+02	9f	-6.100E+02	21b	3.099E+02	21b	2.594E+02
			17f/16f	-4.862E+02	17f/16f	-2.305E+02	12f	2.381E+02		
	P1	P2	P3	P4	P5					
t [s]	0.000E+00	1.198E-03	2.786E-03	4.770E-03	7.174E-03					
λ_e [1/s]	2.042E+03	1.956E+03	1.056E+03	6.483E+02	1.923E+03					
T	1000.0	1001.8	1002.1	1004.8	1039.2					
Tfluc	21b	1.356E+03	21b	1.355E+03	21b	7.914E+02	18f	5.725E+02	1f	2.164E+03
	1f	7.549E+02	1f	7.875E+02	18f	7.681E+02	1f	5.688E+02	9f	-1.782E+03
	9f	-7.541E+02	9f	-7.865E+02	1f	6.527E+02	9f	-5.276E+02	18f	1.427E+03
	18f	6.829E+02	18f	7.453E+02	9f	-6.480E+02	21b	3.336E+02	12f	5.265E+02
			17f/16f	-4.994E+02	17f/16f	-2.454E+02	21b	3.464E+02		

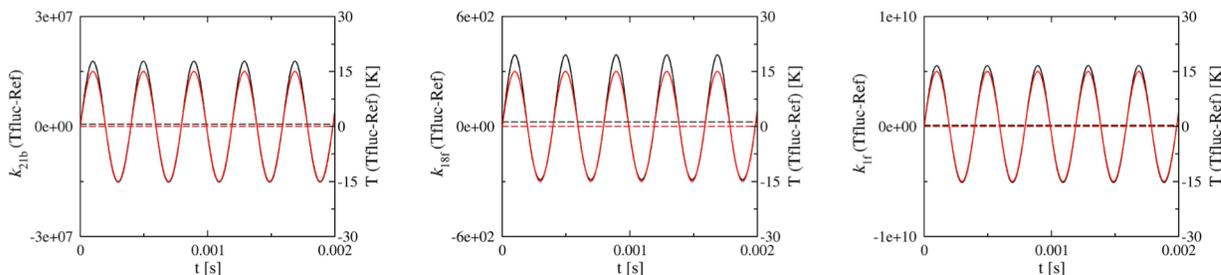


Fig. 4 Reaction rate constants of the important reactions to the explosive eigenvalue in response to the fluctuating temperature. Black and red lines indicate the rate constant and temperature, respectively, and the dashed lines are the mean values.

directly be compared to the reference case at the same point in time.

Initially, at $t = 0$ sec, the largest contributor to the explosive timescale favoring its explosive character, is reaction 21b, decomposing the fuel and forming H and H₂O₂. Additional contributions are provided by reactions 1f and 9f; the first one favors and the second one opposes the explosive character of the explosive timescale, which is reasonable considering that they both compete for each other through the well-known chain branching (1f) and termination (9f) path of H with O₂. It is noted that as a result of this competition, the net effect of these two reactions is insignificant. Finally, the chain branching reaction 18f, which decomposes H₂O₂ to two OH molecules, also provides a smaller contribution, favoring the explosive character of the explosive timescale. Later, at points P2 and P3, the fast explosive timescale decelerates mainly due to the decreasing effect of 21b and the increasing contribution of 16f and 17f, which opposes the explosive character of the explosive timescale, consuming the HO₂ molecules that are necessary for the consumption of the fuel through 21b. The positive effect of reaction 18f gradually increases from P2 to P3 but later on, it starts decreasing; nonetheless, at point P4, it becomes the major contributor to the explosive timescale. Additionally, at point P4, the net effect of the competition between 1f and 9f starts becoming significantly positive due to the increasing effect of reaction 1f as a result of the temperature increase. The contribution of the chain branching reaction 1f, which is a highly endothermic reaction, rapidly increases in the thermal runaway regime and eventually, it becomes the dominant one, as indicated at point P5.

In the fluctuating temperature case, the sets of the reactions contributing the most to the explosive eigenvalue in each point were the same as those in the reference case. However, the contributions of all reactions were slightly increased, the increase of the positive ones being more pronounced, therefore, resulting in a smaller value of the explosive timescale, throughout the whole process. It is noted that the percentage difference of the contribution of each reaction between the fluctuating and the reference cases caused by the temperature perturbation, was similarly increased for all reactions identified by the CSP tool Cs. Considering that the most significant reactions for the evolution of the process, were the same between the fluctuating and the reference case, the effect of the temperature oscillation to the rate constants of

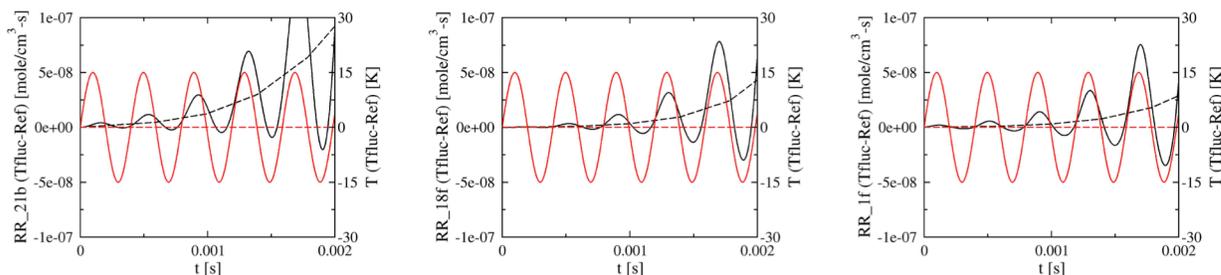


Fig. 5 Reaction rates of the important reactions to the explosive eigenvalue in response to the fluctuating temperature. Black and red lines indicate the reaction rate and temperature, respectively, and the dashed lines are the mean values.

those reactions was investigated.

Fig. 4 displays the difference in the rate constants between the fluctuating and reference cases versus time, overlaid with the difference in the temperature during the first five cycles for reactions 21b, 18f, and 1f. It is shown that the response of the reaction rate constant of 21b, 18f, and 1f is not exactly symmetric against the fluctuating temperature. While the temperature fluctuates in an exact sinusoidal manner such that its mean value is zero, the net effect of the response of the rate constant of 21b, 18f, and 1f over the first cycle is positive. In the next coming cycles, the net positive result of the rate constants of those reactions increases in a cumulative way. This is the main cause of the increase in the reaction rates of those reactions shown in Fig. 5, which eventually leads to larger contributions to the explosive eigenvalue of the system and to a shorter ignition delay time.

5 Conclusions

In the present study, we have investigated the effects of the temperature fluctuations on the ignition delay time for a homogeneous hydrogen-air system. It was found that the ignition delay time was always enhanced when the temperature fluctuation was imposed on the system, regardless of the amplitude and frequency. This phenomenon is due to the non-linear response of the rate constants of the important reactions, as these were identified by CSP. That is, the net result of the rate constants of those reactions is positive, leading to larger reaction rates, which, in turn, lead to larger contributions to the explosive eigenvalue of the system and to a shorter ignition delay time.

Acknowledgement

Research reported in this publication was supported by the King Abdullah University of Science and Technology (KAUST)

References

- [1] Law CK. (2006). *Combustion Physics*. Cambridge University Press
- [2] Bansal G, Im HG, Lee SR. (2009). Auto-ignition of a homogeneous hydrogen-air mixture subjected to unsteady temperature fluctuations. *Combust. Theory Model.* 13:413.
- [3] Sankaran R, Im HG. (2005). Characteristics of auto-ignition in a stratified iso-octane mixture with exhaust gases under homogeneous charge compression ignition conditions. *Combust. Theory Model.* 9:417.
- [4] Kéromnès A, Metcalfe WK, Heufer KA, Donohoe N, Das AK, Sung CJ, Herzler J, Naumann C, Griebel P, Mathieu O, Krejci MC. (2013). An experimental and detailed chemical kinetic modeling study of hydrogen and syngas mixture oxidation at elevated pressures. *Combust. Flame* 160:995.
- [5] Diamantis DJ, Mastorakos E, Goussis DA. (2015). H₂/air autoignition: The nature and interaction of the developing explosive modes. *Combust. Theory Model.* 19:382.
- [6] Valorani M, Najm HN, Goussis DA. (2003). CSP analysis of a transient flame-vortex interaction: time scales and manifolds. *Combust. Flame* 134:35.
- [7] Tingas EA, Kyritsis DC, Goussis DA. (2015). Autoignition dynamics of DME/air and EtOH/air homogeneous mixtures. *Combust. Flame* 162:3263.
- [8] Lam SH, Goussis DA. (1989). Understanding complex chemical kinetics with computational singular perturbation. *Proc. Combust. Inst.* 22:931.
- [9] Lam SH, Goussis DA. (1994). The CSP method for simplifying kinetics. *Int. J. Chem. Kinet.* 26:461.