Effects of H₂ Addition on Flammability Dynamics and Extinction Physics of Dimethyl Ether in Laminar Spherical Diffusion Flame

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ABSTRACT: Flame extinction is one of the most essential critical flame features in combustion because of its relevance to combustion safety, efficiency, and pollutant emissions. In this paper, detailed simulations were conducted to investigate the effect of H₂ addition on dimethyl ether spherical diffusion flame in microgravitational condition, in terms of flame structure, flammability, and extinction mechanism. The mole fraction of H₂ in the fuel mixture was varied from 0 to 15% by 5% in increment. The chemical explosive mode analysis (CEMA) method was employed to reveal the controlling physicochemical processes in extinction. The results show that the cool flame in microgravitational diffusive geometry had the “double-reaction-zone” structure which consisted of rich and lean reaction segments, while the hot flame featured the “single-reaction-zone” structure. We found that the existence of “double-reaction-zone” was responsible for the stable self-sustained cool flame because the lean zone merged with the rich zone when the cool flame was close to extinction. Additionally, the effect of H₂ addition on the cool flame was distinctively different from that of the hot flame. Both hot- and cool-flame flammability limits were significantly extended because of H₂ addition but for different reasons. Besides, for each H₂ addition case, the chemical explosive mode eigenvalues with the complex number appeared in the near-extinction zone, which implies the oscillation nature of flame in this zone which may induce extinction before the steady-state extinction turning point on the S-curve. Furthermore, as revealed by CEMA analysis, contributions of the most dominated species for extinction changed significantly with varying H₂ additions, while contributions of the key reactions for extinction at varying H₂ additions were basically identical.

1. INTRODUCTION

Studies on hydrocarbon fuel combustion are of great significance in improving flame stability, maximizing energy conversion efficiencies, and minimizing the environmental impacts of combustion systems.¹ Flame extinction is not only a crucial near-limit phenomenon in combustion that is challenging in theory but also of great importance for the practical combustion systems. For instance, because the low calorific value gas (such as biogas and landfill gas) has low adiabatic flame temperature, low burning velocity, and high radiant heat loss because of the presence of massive diluents (such as CO₂ and N₂) in fuel gas, the flame resistance to extinction was rather weaker than the methane flame.²,³ Additionally, flame quenching is a common occurrence in microscale combustion devices (such as micro gas turbine and micro thermo-photovoltaic applications) because of the excessive depletion of reactive radicals at the combustor walls.⁴,⁵ Therefore, studies on flame extinction may be valuable for the design of extinction-resistant combustors. Until now, it is widely acknowledged that the strong coupling of chemical kinetics with diffusive transports was responsible for flame extinction.⁶ However, many research studies have shown that the complexity of extinction increased with the number of carbon atoms in the fossil fuel.

Extensive studies have shown that some hydrocarbon fuels and oxygenated fuels are featured by complex reaction kinetics because of the cool-flame chemistry which plays a crucial role in the near-limit flame dynamics (such as extinction and ignition). Sohn et al.⁷ experimentally and numerically investigated the two-stage ignition of n-heptane and discovered that the total ignition delay was mostly governed by the first-stage auto-ignition associated with the cool-flame reactions. Additionally, the existence of cool flame greatly increased the complexity of extinction. Lin et al.⁸ studied the dimethyl ether (DME) diffusion flame extinction limits at elevated pressure and temperature in the counterflow geometry. They reported that the DME diffusion flame had multiple combustion modes.

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and extinction/ignition modes over a wide range of stretch rates; for instance, when the hot flame approached the stretch extinction limit, the hot flame will extinguish and then transition to the cool flame. Inversely, the cool flame can ignite to the hot flame at the ignition limit. Similarly, during the microgravitational \( n \)-alkane droplet flame extinguishment experiments (FLEXs), there also existed the dual-mode behavior for droplet burning and extinction. Specifically, after the droplet ignition by hot-wire, the \( n \)-alkane droplet first exhibited a typical high-luminosity, strong-burning mode which was governed by high-temperature chemistry. A few seconds later, the high-temperature droplet flame started to extinguish because of excessive radiation dissipation, then followed by a lengthy period of a quasi-steady, invisible cool-flame burning mode which was controlled by low-temperature chemistry. When the droplet approached the critical diameter, the cool-flame mode extinguished abruptly, leaving the remaining unburned droplet to continuously vaporize in the quiescent environment. In summary, the FLEX experiments indicate that the conventional flammability limit may need to be redefined because most of the transportation fuels are characterized by cool-flame chemistry.

Additionally, the cool flame sustained by the low-temperature heat production had the nature of weak activation energy, which was distinctively different from the high-temperature chemistry with strong activation energy. As a consequence, the cool-flame structure has a relatively broader reaction zone as compared to the hot flame. Furthermore, the low-temperature chemistry usually tends to have a strong coupling with the flow or solid boundary because of the slow reaction rate, which plays as the fundamental physics of complicity associated with cool-flame combustion. More importantly, many relevant studies have shown that in the cool-flame regime, the fuel oxidation process exhibits the negative temperature coefficient (NTC) behavior in which the low-temperature reactivity slows down with the increasing temperature within a particular temperature range. Law and Zhao investigated the impact of NTC chemistry on ignition in the homogeneous system. They pointed out that the response of total ignition delay time with respect to the initial mixture temperature exhibited the nature of nonmonotonic change, and the two-stage ignition only occurred in the NTC regime.

It is widely accepted that the cool-flame reactions had a profound impact on the global combustion process. Regardless of the trivial heat release rate (HRR) because of the low-temperature reactions, the intermediate hydrocarbon radicals produced in the cool-flame pathway play a significant role in enhancing the high-temperature ignition, turbulent flame propagation, and lift-off stability. The flammability range of combustion can be extended considerably because of the cool-flame chemistry in either homogeneous or spatially diffusive combustion systems. Besides, in the practical engine condition with elevated pressure and mixture preheating, the cool-flame chemical kinetics increased, and thus, its chemical timescale became comparable or even smaller than the engine combustion or turbulence timescales, which resulted in a strong interaction between the cool-flame chemistry with the engine combustion process. The extremely short timescale of cool-flame chemistry will lead to an auto-ignition propagating front in the cylinder which governs the overall fuel ignition and combustion process. Additionally, the knocking wave formation associated with cool flame reactions is the culprit of the “engine knock” phenomenon. Hence, adjustment and control of the cool-flame reactions are crucial for improving the engine performances, which merits a study with sufficient details.

Fuel additive with different functional groups can be used as an efficient blending agent to improve the combustion characteristics of transportation fuels with cool-flame chemistry. \( \mathrm{H}_2 \) with a simple molecular structure and thus free of low-temperature chemistry is often used as a neat fuel or additive to conquer problems associated with the transportation of hydrocarbons. Given the low ignition energy and high burning rate of \( \mathrm{H}_2 \), the relevant studies suggested that blending the hydrocarbon fuels with a trace amount of \( \mathrm{H}_2 \) could increase the flame temperature, reduce the pollutant emissions, extend the lean burning flammability limit, and improve the ignition behavior. Hence, it is reasonable to expect that the \( \mathrm{H}_2 \)-blended fuel may exert ultrasuperior properties. However, the existing studies on hydrocarbon fuels with \( \mathrm{H}_2 \) addition were mainly focused on pollutant emission behavior and ignition behavior. To the best of our knowledge, there were few reports about the effect of \( \mathrm{H}_2 \) addition on the extinction mechanism of transportation of hydrocarbon fuels. Cuoci et al. numerically studied the extinction dynamics of counterflow, laminar, and premixed flames fed with a mixture of methane and \( \mathrm{H}_2 \). They concluded that the extinction limit could be significantly extended due to \( \mathrm{H}_2 \) addition. They paid major attention to the dynamics of the hot-flame extinction; however, examinations of the detailed chemical kinetics that controlled the extinction were rarely involved. Considering the strong effectiveness of cool-flame chemical kinetics and physical dynamics on the global combustion process, the extinction mechanism and underlying physics of cool flames merits a deeper study.

The present study focuses on flammability and extinction dynamics of the DME/\( \mathrm{H}_2 \) blended fuel using the microgravitational spherical diffusion flame (SDF) as the target physical configuration because of its pronounced advantages over the other configurations, including the counterflow flame, droplet flame, and freely propagating flame. First, the SDF is a well-defined physical model for the burning droplet in spray flames, but it can eliminate the heat feedback from flame front to the droplet surface that would influence the fuel vaporization rate by supplying the fuel mixture into quiescent air from the spherical point source at a constant mass flux. Second, the buoyancy-free characteristics in the microgravity condition can eliminate buoyancy-driven flows, which reduces the complexity of analysis significantly. Third, the reduced dimensionality of this flame enables the employment of one-dimensional (1-D) numerical models with high computational efficiency, thus the major attention could be paid onto the most important physicochemical processes that we are interested in.

Furthermore, an attractive alternative fuel DME (\( \mathrm{CH}_3\mathrm{OCH}_3 \)) was selected as the target fuel for the present numerical simulations. DME has a smaller chemistry mechanism size because of its much simpler molecular structure. However, it also has a strong NTC chemistry subset as the large alkanes like \( \mathrm{n} \)-heptane, which facilitates our investigation on the cool-flame dynamics. Besides, the present work is focused on the effect of \( \mathrm{H}_2 \) addition on the extinction dynamics for both hot and cool DME SDF. Because \( \mathrm{H}_2 \) addition showed the most effectiveness in the moderate range (from 0 to 15%), this range of \( \mathrm{H}_2 \) addition was involved.
in this study to investigate its influence on the DME extinction process systematically.

More recently, to identify critical flame features, including ignition, extinction, and stabilization mechanisms, some computational flame diagnostics such as sensitivity analysis, computational singular perturbation (CSP), and chemical explosive mode analysis (CEMA) are proposed as systematic tools to extract important information from the simulation results, particularly involved with the detailed chemical kinetic mechanism. Among these diagnostic tools, CEMA which is based on the eigenanalysis of the Jacobian matrix of the chemical source term in governing equations is most useful in understanding the flame limit phenomena, and its effectiveness was verified in detecting the complicated interactions between chemistries in the multicomponent perfectly stirred reactor (PSR) combustion systems. Thus, CEMA was employed for the present study.

2. DESCRIPTIONS OF THE SIMULATIONS AND CEMA DIAGNOSTICS FORMULATIONS

2.1. Simulation Details. In the present study, a 1-D SDF model was employed for the extinction study. The details of this model, including governing equations with its boundary conditions and numerical methods, were described in our previous study. Here, we just give a brief presentation. As schematically shown in Figure 1, the SDF can be readily established on the spherical porous burner under microgravitational conditions. The fuel mixture was issued from the burner surface with a fixed initial temperature (300 K) and exit velocity (13.0 cm/s) to the quiescent ambient oxidizer mixture (O2/He, 450 K). Because the neat fuel could not be fully oxidized due to the limited diffusion flux of O2, the fuel was diluted by a large fraction of argon (Ar) in order to obtain a stable SDF. The quiescent ambient oxidizer was diluted by a large fraction of the light-density helium (He), which lowered stable SDF. The quiescent ambient oxidizer was diluted by a large fraction of argon (Ar) in order to obtain a matrix of the chemical source term in governing equations.

As described in ref 32, the flammability and extinction dynamics of SDF can be examined by a marching analysis of the S-curve. In current paper, the flame extinction was initiated by lowering the ambient oxygen mole fraction (X02) from pure oxygen until extinction. During simulations, the environment pressure (0.3 atm), fuel exit velocity (13.0 cm/s), temperature (300 K), and the ambient temperature (450 K) remained unchanged. The SDF program first calculated a hot SDF (which was regarded as start flame for flame-controlling continuation) at pure oxygen condition. Subsequently, a flame-controlling continuation method developed by Nishioka was coupled on SDF program to capture a typical singular behavior near the extinction/ignition points on the S-curve (which exhibits the response of maximum temperature with respect to X02), thus allowing for accurate definition of the extinction limit. In this approach, the SDF code was moderately modified by imposing an inner boundary condition (with a prescribed temperature or mass fraction of a specific species) at one inner grid point. Then, the value of X02 was determined by solving an additional dummy equation that is defined based on the unknown variable X02, rather than imposed as an ambient boundary condition. It is noted that the continuation computation is based on steady-state equations.

2.2. Validation of the Computational Model. To validate the accuracy of the computational model, case 1 (0% H2 addition) was assumed as a reference case, the numerical results of temperature profile and some major species profile have been compared with the experimental data from ref 32 which was established at ambient oxidizer composition of 50% O2/50% He under hot flame condition. As shown in Figure 2a, it was analyzed that the predicted...
temperatures of hot flame coincided reasonably well with the measured ones, except for those in the high-temperature zone ($T > 1200$ K). Because, in this region, there was a non-negligible heat loss by radiation and convection from the thermocouples to the ambient during the measuring process. In addition, it can be seen in Figure 2a,b that the measured O$_2$, CO, and H$_2$ mole fractions were slightly lower than the predicted results, and the measured CO$_2$ mole fractions were slightly higher than the predicted results. It is demonstrated that the predicted results agree reasonably well with the experimental data, indicating that the current models could capture flame behavior of DME SDFs accurately. Hence, they were adopted to simulate the other cases of flames in the present work.

2.3. Basic Theory of the CEMA Method. CEMA devotes special attention to the diagnostics on the chemical properties of the mixtures. While some concepts and methods from CSP were applied in the formulation of CEMA, CEMA$^{26-30}$ primarily performs an eigenvalue analysis of the chemical Jacobian for the chemical source term of the reacting flow governing equations. It could clearly reveal the intrinsic chemical kinetics that controls extinction or ignition by identifying the chemical explosiveness of the local mixture, with an assumption that it is placed in a lossless isolated environment. In the theory of CEMA, a general chemically reacting system is expressed using a vector equation form in the Lagrange coordinate system as the following ODES:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) = \mathbf{\omega}(\mathbf{y}) + \mathbf{s}(\mathbf{y}) \quad \mathbf{y} = [Y_1, Y_2, \ldots, Y_K, T]^T$$

(1)

$$J_i = J_{\omega} + f_i = \frac{\partial \mathbf{g}(\mathbf{y})}{\partial \mathbf{y}}, \quad J_{\omega} = \frac{\partial \mathbf{\omega}(\mathbf{y})}{\partial \mathbf{y}}, \quad f_i = \frac{\partial \mathbf{s}(\mathbf{y})}{\partial \mathbf{y}}$$

(2)

where $\mathbf{y}$ is the vector of dependent variables, including all species concentrations and temperature. $\mathbf{\omega}(\mathbf{y})$ is the chemical source term, and $\mathbf{s}(\mathbf{y})$ the nonchemical term, for example, mixing. In the current paper, the bolded symbols indicate vector (dimension $K + 1$) or the Jacobian matrix [dimension $(K + 1) \times (K + 1)$], and the other symbols indicate scalars. All information of the reacting flow system is completely encoded in the full Jacobian matrix, $J_{\omega}$ which is of significance to study the underlying physicochemical processes correlated with flame stability. Analogously, the chemical Jacobian matrix $J_{\omega}$ includes all chemical descriptions of the local mixture, which is helpful to determine the flame dynamics involving detailed chemical reaction mechanisms. It is noticed that the chemical Jacobian matrix $J_{\omega}$ is a block diagonal structure. Because the chemical reaction source term at a given grid point only has a dependence on the local mixture concentrations and temperature, dimension of the $J_{\omega}$ matrix at each grid point is $(K + 1)$ by $(K + 1)$. Thus, the CEMA method could be carried out grid by grid and is rather high efficient. In this work, a numerical perturbation method was used for the calculation of the $J_{\omega}$ matrix, which exhibited superior accuracy and reliability.

For the sake of simplicity, the formula 1 is transformed to formula 3 where the $s(y)$ in $g(y)$ is negligible. If a simple eigendecomposition is employed on $J_{\omega}$ (formula 4), the formula 3 can be further transformed to formula 5. Where the diagonal matrix $\mathbf{A}$ consists of the eigenvalues of $J_{\omega}$, $\mathbf{A}$ and $\mathbf{B}$ represent the corresponding left and right eigenvectors, respectively.

$$\frac{d\mathbf{\omega}}{dt} = J_{\omega} \mathbf{\omega}$$

(3)

$$J_{\omega} = \mathbf{V} \cdot \mathbf{\Lambda} \cdot \mathbf{V}^{-1} = \mathbf{A} \cdot \mathbf{\Lambda} \cdot \mathbf{B}$$

(4)

$$\frac{df}{dt} = \mathbf{A} \cdot \mathbf{f}, \quad \mathbf{f} = \mathbf{B} \cdot \mathbf{\omega}$$

(5)

$$f_i = f_{i,0} \cdot e^{\lambda_i t}, \quad f_i = b_i \cdot \omega_i, \text{ when } t = 0, \; f_i = f_{i,0}^{(i = 1, 2, \ldots, K + 1)}$$

(6)

Obviously, there are $(K + 1)$ independent solution variables in eq 5, as shown in formula 6. Each solution variable $f_i$ is defined as a chemical mode, $\lambda_i = b_i J_{\omega} a_i$ is the $i$th eigenvalue of $J_{\omega}$ and $b_i$ and $a_i$ correspond to left and right eigenvectors associated with $\lambda_i$ respectively. Because of the energy and element conservations, chemical Jacobian $J_{\omega}$ always includes $M + 1$ conservative chemical modes, where $M$ is the total number of participating elements. Therefore, such $(M + 1)$ conservative modes with zero eigenvalues are readily identified and excluded in the candidate chemical mode list, then leading to $(K-M)$ nonconservative modes. The eigenvalues’ real part of remaining nonconservative modes are sorted in the decreasing order. The first nonconservative chemical mode with the largest positive eigenvalue is referred to as the chemical explosive mode (CEM), that is
\[
\text{Re}(\lambda_e) > 0, \quad \lambda_e = b_e^* a_e \tag{7}
\]
where the subscript e indicates the explosive mode. Note that in the present study, the operator \(\text{Re}(\cdot)\) returns the real part of a complex number.

The occurrence of a CEM with a positive eigenvalue means that the local mixture is characterized by their chemically explosive nature, that is, if the mixture is placed in an isolated, nondissipative environment, the reaction rates tend to rise exponentially along the direction of the eigenvectors associated with the CEM, which will evolve to thermal runaway or ignition. Many research studies showed that the shift of a CEM from explosive \([\text{Re}(\lambda_e) > 0]\) to nonexplosive \([\text{Re}(\lambda_e) < 0]\) is highly relevant to some critical flame features, including ignition, extinction, and premixed flame propagation.\(^{25,28}\) Therefore, an explosion index \((\text{EI})\)\(^{26-30}\) is defined to quantitatively evaluate the crucial chemical kinetics that governs the limit flame phenomena.

\[
\text{EI} = \frac{\text{diag}(a_e^* b_e)}{\text{sum diag}(a_e^* b_e)} \tag{8}
\]
where the operator \(\text{diag}(\cdot)\) returns the diagonal elements of a matrix; vector \(\text{EI}\) is a normalized vector with each entry varying within \([0, 1]\), which indicates the normalized contribution of chemical species or temperature to the CEM.

A larger entry close to unity indicates that the corresponding species or temperature is dominant in the extinction dynamics that are strongly associated with CEM.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effects of H\(_2\) Addition on the Structure of DME Hot and Cool SDFs

Our previous study\(^{31}\) has indicated that in each H\(_2\) addition case, both a strongly burning hot-SDF and a weakly burning cool-SDF could be readily established over a broad range of the ambient oxygen mole fraction \((X_{O_2}^a)\), as shown in Figure 5. Some representative hot flames (established at \(X_{O_2}^a = 42.1\%\)) and cool flames (established at \(X_{O_2}^a = 23.2\%\)) at various H\(_2\) addition cases were selected for examining the influence of H\(_2\) addition on the structure dynamics of the hot and cool SDFs, respectively, and the results are shown in Figures 2 and 3. In this work, the isocontour YOH = 0.2YOH, \(\text{max}\), and the CH\(_3\)OCH\(_2\)O\(_2\) mass fraction profile were used to determine the border of the hot-flame reaction zone and cool-flame reaction zone, respectively.\(^{38}\) Figure 3 shows that the hot-flame chemistry with a strong dependence on temperature was typically limited to a finite reaction zone because of its high activation energies, while Figure 4 shows that the cool flames had a dramatically broader reaction zone and thus a larger radius than that of hot flames, resulting in the rather smaller dissipative loss (longer residence time). This is because the cool-flame chemistry had the nature of low activation energies, implying that the reaction zone situated itself to expand to a much wider radius because of the weak temperature dependence. It was demonstrated that the existence of SDF cool flame was largely ascribed to the abrupt expansion of flame radius in the low-temperature condition and thus the significant increase of the residence time. Hence, cool flames could be self-sustained, although the rates of low-temperature reactions were rather depressed. Moreover, for either H\(_2\) addition case, the employment of the local mixture equivalence ratio \((\phi_{\text{local}})\) as defined in formula 9 where \(K\) is the total number of species, and \(X_k\) is the molar fraction of \(k\)th species \(\text{C}_n\text{H}_k\text{O}_l\) indicates that the hot-flame chemistry occurred near the chemical stoichiometry location \((\phi_{\text{local}} \approx 1\).

\[
\phi_{\text{local}} = \frac{\sum_{k=1}^{K} [2m + n/2]X_k}{\sum_{k=1}^{K} (2X_k)} \tag{9}
\]

Unlike hot flames, it was found that the cool flame with a double-reaction-zone structure had the feature of both premixed and nonpremixed combustion (as shown in Figure 4b), including one located on the fuel side (rich region: \(\phi_{\text{local}} > 2.8\)) which dominates the majority low-temperature heat release, and the other located on the oxidizer side (lean region: \(\phi_{\text{local}} < 0.6\)) with marginal heat release. The previous study of DME premixed flame in a planar freely propagation condition also reported that the self-sustained cool flame could only exist in fuel-lean or rich regions but not in the stoichiometric condition.\(^{16}\) In summary, H\(_2\) addition exerted a pronounced effect on the structure of DME SDF, and it should be noted that H\(_2\) addition affected cool flames much more than hot flames in terms of flame radius, reaction zone width, HRR, pollutant emissions, temperature, and so forth, which has been discussed in more details in our previous publication.\(^{31}\) Here, we just make a supplementary discussion.

As shown in Figure 4a, it is interesting to note that with the increase in H\(_2\) addition, the fuel-rich HRR of cool flame was depressed due to DME dilution,\(^{31}\) while the fuel-lean HRR was slightly enhanced, this is because \(\text{O}_2\) played an important role in the low-temperature exothermic reactions, and H\(_2\) addition promoted the mixing of O\(_2\) and radicals within the fuel-lean region, thus leading to a slightly raised HRR. Additionally,
Figure 4. Cool-flame structures at the ambient oxygen mole fraction $X_{O_2} = 23.2\%$ for cases 1–4: the profiles of temperature ($T$) and HRR ($a$); profile of CH3OCH2O2 mass fraction ($b$).

Figure 4b shows that regardless of H2 addition, the location and width of the fuel-rich region were quite insensitive to H2 addition and remained nearly unchanged (within $x = 0.95–2.6$ cm); however, the fuel-lean region with a feature of premixed combustion moved inward along the radial direction with increasing H2 addition because of its enhanced low-temperature chemistry and thus raised flame propagation speed. In summary, the impact of H2 addition on the cool-flame structure was much more complex than on the hot-flame structure, and the role of H2 addition in affecting the cool-flame combustion process merits further investigation.

3.2. Effects of H2 Addition on the Flammability Limit and Extinction Physics of DME Hot and Cool SDFs. The SDF extinction and ignition dynamics can be characterized in terms of the $S$-curve which consists of stable hot- and cool-flame branches, as well as physically unstable branches. The hot and cool flames are highly correlated to the strongly burning and the weak-reacting states, respectively. Figure 5 shows the response of the maximum flame temperature with respect to the variation in ambient $X_{O_2}$ under different H2 addition cases, which is characterized by the $S$-curves. In our previous study,31 we have discussed the impact of H2 addition on $S$-curve behaviors of the DME SDF, and here we just make a brief description. It is seen in Figure 5 that the hot-flame extinction limit slightly extended with increasing H2 addition ($X_{O_2}^* = 23.2, 22.0, 20.5,$ and $19.1\%$ for cases 1–4, respectively), while H2 addition caused the shrinkage of the cool-flame extinction limit ($X_{O_2}^* = 5.3, 5.7, 6.2,$ and $7.2\%$ for cases 1–4, respectively). Additionally, the cool flame could shift to the hot flame by ignition at a sufficient level of $X_{O_2}^*$ ($X_{O_2}^* = 77.9, 86.1,$ and $89.5\%$ for cases 1–3, respectively), even though the $X_{O_2}^*$ level was within the hot-flame flammability range. This hysteresis effect associated with the hot and cool flame inter-transition was also found in the PSR fed with a mixture of rich DME/air.30 However, Figure 5 shows that when H2 addition was $15\%$ or more, the cool flame could not recover back to hot flame even in pure oxygen ($X_{O_2}^* = 100\%$), revealing that H2 addition caused great difficulty in the shift from the cool-flame mode to hot-flame mode.

As reported in ref 31, compared with the cool flame, the hot-flame temperature was more sensitive to the ambient oxygen concentration. It can be seen from Figure 5 that H2 addition led to a steeper slope of hot-flame branches and a flatter slope of cool-flame branches, which implied that H2 addition further increased the sensitivity of hot-flame temperature to $X_{O_2}^*$ but further decreased sensitivity of cool-flame temperature to $X_{O_2}^*$. Moreover, marching analysis along each $S$-curve revealed that compared with hot flame, the cool-flame structure significantly varied with decreasing $X_{O_2}^*$; for example, Figure 6 shows distributions of the HRR branches of hot and cool flames in the normalized radial direction space for case 2. It is clearly demonstrated that for the cool-flame branch (as shown in
Figure 6b), the fuel-rich HRR branch \( (\phi_{\text{local}} > 2.8) \) was responsible for the majority of exothermicity, while the fuel-lean HRR branch \( (\phi_{\text{local}} < 0.6) \) had marginal exothermicity. It was further found that when the cool flame was approaching the extinction tuning point by decreasing \( X_{O_2}^* \), the fuel-lean HRR branch and fuel-rich branch moved toward each other, and eventually, the lean HRR branch merged with the rich HRR branch. Hence, the disappearance of two-reaction-zone can serve as a judgement criterion for the cool-flame extinction.

To better understand the underlying physics of extinction, CEMA analysis was applied to the continuation results along the \( S \)-curve (Figure 5), with the color at each circle point indicating the logarithmic eigenvalue of the CEM mode at the maximum temperature location of each flame; the profile of flame temperature for representative state points P1–P5 and P7–P8 on the \( S \)-curve of case 2 (b), the color at each data point indicates the logarithmic eigenvalue of the CEM mode at the corresponding grid point.

Figure 6. Evolvement of hot-flame HRR (a) and cool-flame HRR (b) on the \( S \)-curve in the radial direction space for case 2. \( x \) represents distance away from the burner surface; \( r_b \) represents burner radius; and superscript "*" represents ignition/extinction limits. \( X_{O_2}^* = 22.0\% \) in the left figure represents the hot-flame extinction limit and \( X_{O_2}^* = 5.7 \) and 86.1\% in the right figure represents cool-flame extinction and ignition limits, respectively.

Figure 7. \( S \)-curve of case 2 which was sampled from Figure 5 (a), the color of each state point along the \( S \)-curve indicates the logarithmic eigenvalue of the CEM mode at the maximum temperature location of each flame; the profile of flame temperature for representative state points P1–P5 and P7–P8 on the \( S \)-curve of case 2 (b), the color at each data point indicates the logarithmic eigenvalue of the CEM mode at the corresponding grid point.

To better understand the underlying physics of extinction, CEMA analysis was applied to the continuation results along the \( S \)-curve (Figure 5), with the color at each circle point indicating the logarithmic eigenvalue of the CEM mode at the maximum temperature location of each flame. Figure 5 shows that for each \( H_2 \) addition case, with respect to the strongly stable hot flames that were located far away from the hot-flame extinction turning points, there was no strong CEM within the reaction zone; instead, all nonconservative chemical modes had negative eigenvalues, which implied that the reaction mixtures achieved the chemical equilibrium state. In the CEMA theory,\(^{27-30}\) the timescale of a chemical mode could be approximately evaluated by the corresponding reciprocal eigenvalue, that is, \( \tau_e = \left| \text{Re}(\lambda_e) \right|^{-1} \). Considering the fact that the nonconservative mode with the largest negative eigenvalue (namely the shortest timescale) governed the global reaction rates that were approaching the equilibrium; therefore, for the nonexplosive hot flames, the dominant nonconservative mode with the largest \( |\lambda_e| \) was defined as CEM. It is seen in Figure 5 that for either \( H_2 \) addition case, the large negative eigenvalues at the maximum temperature location of strongly stable hot flames indicated that the stoichiometric mixture was nonexplosive (blue circle). However, when the hot flame was approaching the extinction, \( \lambda_e \) at the maximum temperature location became positive abruptly, which means that the stoichiometric mixture property inside the flame shifted from nonexplosive to explosive. Hence, it is safe to suggest that zero-crossing of the dominant eigenvalue or appearance of the positive CEM mode can play as a robust judgement for the tendency to extinction. This study showed that as \( H_2 \) addition increased from 0 to 15\%, the \( \lambda_e \) zero-crossing points decreased from \( X_{O_2}^* = 34.7 \) to 25.3\%, further indicating that \( H_2 \) addition was considerably favorable to the hot-flame stability and flammability limit.
Additionally, marching analysis was conducted along the hot-flame branches, revealing that as the hot flame passed through the \( \lambda_e \) zero-crossing points, some important high-temperature chain-branching reactions (e.g., R1: \( \text{H} + \text{O}_2 = \text{O} + \text{OH} \), R30: \( \text{HCO} + \text{M} = \text{H} + \text{CO} + \text{H} \)) dropped more rapidly than the chain-termination reactions (e.g., R17: \( \text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2 \), R51: \( \text{CH}_4 + \text{HO}_2 = \text{CH}_2\text{O} + \text{OH} \)). This indicates that the hot-flame extinction was accompanied by strong competition between branching chemistry and termination chemistry, which will be further discussed in detail in Section 3.3. At the meantime, some hydrocarbon intermediates (such as \( \text{CH}_3\text{CHO}, \text{CH}_2\text{HCO}, \) and \( \text{CH}_3\text{OCH}_2\text{OH} \)) responsible for the explosiveness and ignitiveness started to emerge. Hence, it was reasonable to infer that the appearance of positive \( \lambda_e \) associated with the ignitive mixture resulted from incomplete fuel decomposition in the oxygen deficiency condition. With the further decrease in \( X_{\text{O}_2}^* \), the depression in heat production and increase in mixture heat capacity because of the incomplete fuel oxidation caused a rapid decrease in the flame temperature, which finally led to flame extinction. Likewise, the CEM with large positive \( \lambda_e \) at the maximum temperature location was also detected near the cool-flame extinction and ignition turning points (as shown in Figure 5). To further elaborate the flame structure, case 2 is assumed as a reference case (because other cases are quite similar); some representative state points of S-curve were selected as investigated flames (hot flames: P1–P5 and cool flames: P6–P8, as shown in Figure 7a), and Figure 7b shows the temperature profiles for these representative flames, of which the color superposed to the circle point indicates the logarithmic eigenvalues of \( \lambda_e \) associated with the CEM mode. With respect to hot flames (P1–P5), it is evident that at relatively higher level \( X_{\text{O}_2}^* \) (namely, P1 and P2), \( \lambda_e \) in the core reaction zone had large negative values, revealing that the majority of heat release was confined to this subzone owing to the high-temperature postignition mixture. Furthermore, we also detected trivial positive \( \lambda_e \) in the subzone upstream of the core reaction zone, indicating that there existed low-temperature reactions at rather weak rates in this low-temperature subzone. However, zero–\( \lambda_e \) which was defined as the dormant mode, was dominated in other subzones, revealing that the combustion reaction in these subzones almost ceased. Besides, it can be seen in Figure 7b that when \( X_{\text{O}_2}^* \) approached zero-crossing point (such as P3 curve), a CEM mode with large positive eigenvalues first occurred at the maximum temperature location, meaning that the mixture explosiveness started to be enhanced because of oxygen deficit. Subsequently, as the \( X_{\text{O}_2}^* \) further decreased, the width of the positive CEM profile gradually expanded (such as P3–P5). Moreover, it should be noted in Figure 7b that for the hot flames, strong CEM only appeared near the extinction region (e.g., P3–P5), while for cool flames, there always existed strong CEM with positive eigenvalues in both rich and lean regions (e.g., P6–P8). This is expected because the cool-flame structures controlled by the low-temperature competing kinetics were far away from the chemical equilibrium. Moreover, for cool flames, Figure 7b shows that the CEM profile could well represent the double-reaction-zone structure.

Additionally, we had observed the complex eigenvalues within the near-extinction region on hot- and cool-flame branches, even the imaginary part of the complex eigenvalue may exceed the real part. From the viewpoint of mathematics, the complex eigenvalues usually indicated that the chemical mode was characterized by their oscillatory nature,17 with the real part controlling oscillation amplitude and the imaginary part controlling oscillation frequency. Therefore, it is reasonable to infer that hot- and cool-flame extinctions were probably accompanied by some degree of oscillation. In comparison with the hot flame, the cool-flame oscillations were more prone to occur because the cool-flame chemistry had the strong coupling with transports or solid boundaries because of the low scalar dissipation rate.13 To quantitatively validate the above conclusions, case 2 is assumed as a reference case; some near-extinction steady-state hot flames were sampled from the S-curve of case 2 (such as T1–T5 in Figure 8a); then, a small temperature perturbation (\( \delta T \)) was imposed on these hot flames, and the transient response will be examined to investigate the oscillation dynamics. Figure 8b shows the transient responses of these flames with respect to a small temperature perturbation. It should be noted that the temperature perturbation was imposed on the steady-state solution at the initial time \( t = 0 \) and turned off during the transient simulations, and hence, the oscillation as well as its frequency were the inherent nature of the flame.

As shown in Figure 8b, when \( X_{\text{O}_2}^* \) decreased from 24.21 to 22.11% gradually, the oscillation amplitude rapidly increased because of increased Re(\( \lambda_e \)), and meanwhile, the oscillations transitioned from physically stable to unstable. It can be seen that the flames at \( X_{\text{O}_2}^* = 24.21\% \) (T1 flame) and 22.84% (T2 flame)
were physically stable because they eventually converged to the initial steady-state; however, the flames at $X_{O_2} = 22.63\%$ (T4 flame) and $22.11\%$ (T5 flame) were unstable because they finally evolved to extinction, although they existed within the hot-flame flammability range on the $S$-curve of case 2 (as shown in Figure 8a). It is further seen that the perturbation for T1 and T5 flames rapidly decayed without oscillations, while that for T2 and T4 flames decayed with several cycles of oscillation. This is because the $\lambda_e$ at the maximum temperature location of T1 and T5 flames were the real number, while that of T2 and T4 flames were the complex number. Hence, it can be inferred that there existed an oscillation range on either hot- or cool-flame branch of the $S$-curve in which the $\lambda_e$ at the maximum temperature location was a complex eigenvalue. Additionally, it was oscillated with a persistent amplitude which did not develop to extinguishment for a fairly long time. This study further concluded that the practical flame extinction occurred prior to the extinction turning points of $S$-curves for either hot flames or cool flames.

### 3.3. Effects of $H_2$ Addition on the Extinction Mechanism of DME Spherical Diffusion Hot and Cool Flames

As mentioned earlier, the occurrence of extinction is mainly ascribed to the coupling of chemical kinetics with transports. Mathematically, there existed a singular full Jacobian matrix $J_e (J_e = J_m + J_s)$, where $J_m$ indicates a mixing Jacobian matrix featured with zero eigenvalues at the extinction turning points on the $S$-curve (such as P5 and P8, as shown in Figure 7a). Nevertheless, the sum of $J_m$’s positive CEM eigenvalues with corresponding $J_s$’s negative eigenvalues equals zero. Therefore, the chemical timescale balanced with mixing timescale (or $Da = 1$) at the bifurcation turning points. Additionally, it was
found that when the flame was very close to extinction turning points on the S-curve, the eigenvalue of J_\lambda remained nearly unchanged, while that of J_\lambda, significantly increased owing to the sharp decrease in mixture temperature. Hence, zero-crossing of a full Jacobian matrix J_\lambda's eigenvalue at the bifurcation turning points on the S-curve was primarily attributed to the sharp increase in Re(\lambda_\lambda) as shown in formula 10.

\[
\text{Re}(\lambda_\lambda) = \text{Re}(b_{\lambda} \cdot J_\lambda \cdot a_{a}) = \sum_{i=1}^{I} \text{Re}(b_{\lambda} \cdot J_\lambda \cdot a_{a}) = \sum_{i=1}^{I} \text{Re}(\lambda_i)
\]

where I indicates the total number of elementary reactions, and J_\lambda is the chemical Jacobian which denotes the contribution of the rth reaction to J_\lambda. \lambda_\lambda denotes the contributing eigenvalue because of the rth reaction. As a consequence, a bifurcation index (BI_\lambda)^{30} was employed to reveal the contribution of the rth reaction to extinction, as defined in formula 11. BI_\lambda is normalized to [-1, 1]. A reaction with large |BI_\lambda| plays a key role in controlling extinction, and BI_\lambda with opposite signs indicates opposite impacts of corresponding reactions on flame extinction.

\[
\text{BI_\lambda} = \frac{\text{Re}(\lambda_i)}{\max_{1 \leq i \leq I} |\text{Re}(\lambda_i)|}
\]

In the following, CEMA detection was applied to identify the key factors controlling extinction at hot- and cool-flame extinction turning points for cases 1–4. Given the absolute dominance of explosive CEM in extinction, we extracted detailed thermochemical information at the mesh point with the maximum Re(\lambda_i) value for CEMA analysis. Figure 9a,b shows the controlling reactions identified by BI_\lambda and controlling species or temperature identified by EI at hot-flame extinction turning points for cases 1–4. Likewise, Figure 10a,b shows the results at the cool-flame extinction turning points for cases 1–4. For each H_2 addition case, it was suggested that both hot- and cool-flame extinction were governed by the complex coupling of heat release/loss with the branching/propagation/termination chemistries.

With respect to the hot-flame extinctions, it is seen in Figure 9a that regardless of H_2 addition, the reaction (R1: H + O2 = O + OH) with the largest positive BI_\lambda, had a most favorable effect on flame stability because of its dominance in the chain-branching chemistry, although the reaction (R1) had endothermic nature. Conversely, the reaction [R53: CH_3 + H (+M) = CH_4 (+M)] with the largest negative BI_\lambda, indicated its largest effectiveness in promoting flame extinction because of its chain-termination nature, although the reaction (R53) had exothermic nature. Besides, the chain-propagation reaction (R29: CO + OH = CO_2 + H) was also rather favorable to flame stability because of its significance in the heat production, and the product H could also participate in the branching reaction (R1) to increase the branching rate. Additionally, it can be seen in Figure 9a that H_2 addition affected the contribution of each key reaction to the hot-flame extinction. For instance, when H_2 addition was 10% or more (cases 3 and 4), the importance of the reaction (R29) to extinction was surpassed by chain-branching (R30) and chain-termination (R56), as indicated by |BI_\lambda| values. This is because the hot-flame temperature increased with increasing H_2 addition, the reactions (R30) and (R56) with high activation energies had a strong dependence on temperature and thus played a more important role in high-temperature regime.

Figure 9b shows the contribution of temperature (heat release) and species to hot-flame stability for cases 1–4. Obviously, regardless of H_2 addition, heat release was most influential to the hot-flame extinction, then followed by the key species CH_4, O_2, and C_2H_2 in descending order based on their EI magnitudes. It was found that as H_2 addition increased, the EI values of T, CH_4, and O_2 gradually decreased, while that of C_2H_2, H_2, CH_3OCH_2, OH, C_2H_2, H_2, and H increased. Especially, the decrease in the EI value of T was most prominent, for instance, when H_2 addition was 15% (case 4), the effect of CH_4 on flame extinction could be comparable to that of T. In summary, H_2 addition moderately affected the key reactions and species controlling hot-flame extinction. Besides, the hot-flame extinction was mainly governed by the competition between high-temperature exothermicity/endothermicy and branching/termination chemistries involving small molecules.

With regard to the cool-flame extinction, it is observed in Figure 10a that H_2 addition exerted a little effect on controlling reactions, implying that the reactions that controlled cool-flame extinction belonged to the DME low-temperature reaction pathway, irrelevant with H_2 addition. As shown in Figure 10a, regardless of H_2 addition, the exothermic reaction (R273: QOOH + O2 = O_2QOOH) was most important to cool-flame extinction, and although its exothermic effect was negligibly small, its beneficial effect for cool-flame stabilization was mainly ascribed to their chain-branching nature. The endothermic reaction (R271: RO_2 = QOOH) also had a favorable effect on cool-flame stability because of its chain-branching characteristics. Because the chain-propagation reaction (R240) had a strong exothermic effect and primarily provided the initial fuel radical (CH_3OCH_2) which was crucial during the initial stage of DME decomposition, (R240) was favorable to cool-flame stability. Similarly, the (R241) was also favorable to cool-flame stability due to the supply of the fuel radical R. Additionally, Figure 10a shows that (R44) and (R42) with negative BI_\lambda were unfavorable to cool-flame stability despite their heat release effect because the intermediate species CH_3O, which played a vital role in sustaining the low-temperature chemistry, was consumed by these two reactions. The reactions (R272) and (R267) had also exothermic effect, but they were unfavorable to cool-flame stability due to their chain-termination nature. Moreover, one interesting observation was apparent from Figure 10a, when DME was blended with H_2 (cases 2–4), the effect of reaction (R42) on cool-flame extinction was slightly greater than that for reaction (R271); however, this effect was rather ignorable.

Figure 10b shows the contribution of temperature (heat release) and species to cool-flame stability for cases 1–4. It is observed that H_2 addition exerted a significant effect on the contribution of controlling species to cool-flame extinction. For case 1, the species CH_2O was most influential to the cool-flame extinction, however, for cases 2–4, the temperature contributed most to cool-flame stability, and the EI value of T increased with increasing H_2 addition. This is because the low-temperature heat release played an important role in extinction, and H_2 addition resulted in the reduced intensity of cool-flame chemistry and hence the heat release. Besides, regardless of H_2 addition, O_2 which played a vital role in the chain-branching pathway (R273) was also significant to cool-flame stability, just behind the T and CH_2O. However, the other governing factors, including CH_3OCH_2, O_2, and CH_2O_2, had a negligible effect on cool-flame extinction.
flame extinction. Hence, the main governing species that controlled cool-flame extinction were \( T, CH_2O, O_2, HO_2CH2OCHO, \) and \( CH_3OCH_3 \) for all cases. In summary, the cool-flame extinction was controlled by the complex competition of low-temperature heat release with chain-branching/termination chemistries involving large molecules.

3.4. Validation for BI and EI Analyses. In the following part, to verified accuracy and reliability of the above results derived from CEMA analyses, case 3 (10% \( H_2 \) addition) is assumed as a reference case, and some governing reactions determined by BI analyses (e.g., hot flame: R1, R29, R30, R53, R56; cool flame: R273, R240, R44, R272) were perturbed, namely, their prefactors were increased by 3.0 times and then recalculating the S-curves to obtain the perturbed extinction limit. Likewise, some governing factors determined by EI analyses (e.g., hot flame: \( T, O_2, CH_4 \); cool flame: \( T, O_2, CH_2O \)) were perturbed, namely their mixture conductivity and the diffusion coefficient were increased by 2.0 times to recalculate the S-curves. Figure 11 compares extinction limits obtained from the original S-curves and perturbed S-curve. With respect to the hot-flame extinction limit, Figure 11a shows that for reactions (R1, R29, and R30) with positive BI, enhancement of their reaction rates could expand the hot-flame extinction limit and thus the flammability range. However, the hot-flame flammability range was obviously shrunk when increasing rates of reactions (R53 and R56) because these reactions had negative BI values. Additionally, Figure 11a shows that \( O_2 \) diffusivity and mixture conductivity had a great influence on the hot-flame extinction limit. Because the combustion process was sustained by the oxygen diffusion into the reaction zone, enhancement of \( O_2 \) diffusion ability could greatly expand the extinction limit and thus increase the stable-branch temperature. However, the increase in mixture conductivity resulted in depressed flame temperature and thus the shrinkage of the flammability range. This is because the heat release in the reaction zone was largely dissipated due to the enhanced conduction. Analogously, with regard to the cool-flame extinction limit, Figure 11b shows that the cool-flame extinction limit could be extended by increasing the rates of reactions (R273) and (R240) or increasing \( O_2 \) and \( CH_2O \) diffusivities. However, enhancements of reactions (R44) and (R272) as well as mixture conductivity reduced the cool-flame temperature and thus were unfavorable to flame stability. In summary, the above parameter study effectively validated the reliability and accuracy of BI and EI analyses based on CEMA.

Additionally, the above BI-based and EI-based methods were compared with the sensitivity analysis method which has been widely employed in the chemical engineering studies in the literature. Here, to reveal the governing reactions or species for extinction, we have proposed a logarithmic sensitivity index (SI) formulation that is defined based on the extinction limit (\( \chi \)).

\[
SI = \frac{\partial \ln(\chi)}{\partial \ln(\alpha)} \approx \frac{\chi - \chi'/\chi}{(\alpha - \alpha')/\alpha}
\]

where \( \alpha \) denotes an arbitrary model parameter (e.g., the reaction prefactor, a species diffusivity, or the mixture thermal conductivity, etc.), and \( \alpha' \) is a perturbed model parameter. \( \chi \) and \( \chi' \) are the extinction limits before and after the parameter perturbation. For simplicity, a normalized SI (NSI = |SI|/max SI) was obtained.
directly quantify important processes controlling critical recomputations. On the contrary, the CEMA method can owing to numerous parameter perturbations and subsequent chemical kinetic mechanism, it is extremely time-consuming analysis. Although sensitivity analysis can also reveal the species for extinction.

factors (such as rth reaction, kth species, and mixture conductivity). By the definition, the governing factor with larger NSI magnitude is more important for the extinction. Here, case 3 (10% H2 addition) is assumed as a reference case for sensitivity analysis. Figures 12 and 13 compare the IBII/NEI and the NSI for the hot-flame extinction limit and the cool-flame extinction limit, respectively. Figure 12 shows that for the hot-flame extinction limit, the IBII and NEI values were nearly correlated with NSI. Similar correlation is also observed in Figure 13 for the cool-flame extinction limit. Therefore, it is evident that the IBII/NEI values could agree fairly well with sensitivity analysis results in detecting governing reactions and species for extinction.

Moreover, CEMA analysis had more virtues than sensitivity analysis. Although sensitivity analysis can also reveal the chemical kinetic mechanism, it is extremely time-consuming owing to numerous parameter perturbations and subsequent recomputations. On the contrary, the CEMA method can directly quantify important processes controlling critical flame phenomena base on the local solution. Hence, it is super-efficient and especially suitable for detecting ignition and extinction involving large and complex mechanisms. More importantly, some additional key information on ignition/extinction can be directly obtained from the CEMA method because of its rigorous mathematical foundation; however, such information cannot be readily derived from sensitivity analysis.

4. CONCLUSIONS

In this work, we studied the effect of H2 addition on DME SDF in hot- and cool-flame conditions, in terms of flame structures, flammability, and extinction mechanisms. The key species and reactions controlling flame extinction were derived from CEMA. The main findings for this study are as follows:

1. Compared with the hot flame, the cool flame had a double-reaction-zone structure. The width and location of the rich reaction zone were independent of H2 addition, while the lean reaction zone moved inward along the radius direction with increasing H2 addition. Additionally, as H2 addition increased, the reaction intensity of rich zone decreased because of the reduced DME concentration in the fuel mixture, while the reaction intensity of the lean zone slightly increased because of strong mixing near the left boundary. Because the cool-flame structure was mainly determined by the rich zone, the HRR and temperature of cool flame decreased with increment in H2 addition.

2. The flammability range of DME SDF could be significantly extended with increasing H2 addition for both hot and cool flames. Interestingly, the extension of hot-flame flammability was ascribed to the decrease in the extinction limit, while the extension of cool-flame flammability was ascribed to the increase in the ignition limit although the cool-flame extinction limit slightly shrank by H2 addition. Furthermore, compared with the cool flame, the hot-flame temperature was more sensitive to the ambient oxygen concentration. H2 addition further increased the sensitivity of hot-flame temperature to XO2flame but further increased insensitivity of cool-flame temperature to XO2flame.

3. For hot flame at sufficiently low XO2flame at each H2 addition case, the CEM with positive eigenvalues initially emerged at the peak temperature location because of incomplete fuel cracking. H2 addition decreased the zero-crossing point of λe on the hot flame branch, which further indicates that H2 addition was favorable to extend the hot-flame flammability limit. With respect to cool flame, the CEM appeared within its two subzones where the flame structure and HRR were rather different. Moreover, within the near-extinction range on either hot-flame or cool-flame branch, the CEM eigenvalues were complex numbers, which means that the near-extinction flame may probably show an oscillation behavior. This makes oscillation-induced extinction occur prior to the steady-state extinction turning point.

4. For either hot- or cool-flame extinction at varying H2 addition, although the dominances of the key reactions and species for extinction remained basically unchanged, H2 addition affected the contribution of these reactions and species to flame extinction. Regardless of H2 addition, the reaction (R1: H + O2 = O + OH) and (R273: CH3OCH2O2H + O2 = O2CH2OCH2O2H) were most influential to hot-flame extinction and cool-flame extinction, respectively. Furthermore, as H2 addition increased, the importance of heat release to hot-flame extinction was depressed (as indicated by the EI value), while that to cool-flame extinction was sharply increased. Overall, the hot-flame extinction was primarily correlated to high-temperature reactions involving small
molecules, while the cool-flame extinction was correlated to low-temperature reactions involving large hydrocarbons.

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**Notes**

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