On Explosion Limits of H₂/CO/O₂ Mixtures

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Abstract: The pressure-temperature explosion limits of H₂/CO/O₂ mixtures were analyzed computationally and theoretically. It is shown that, with the addition of even a minute quantity of H₂, the mixture explosion limits evolve from being monotonic to the non-monotonic Z-shaped response characteristic of H₂/O₂ mixtures. It is further shown that the explosion limit at various conditions can be reproduced well with a reduced mechanism of 12 elementary steps and 10 species. Eigenvalue analysis of this mechanism leads to an analytic solution for the explosion limits, yielding explicit expressions for the degenerate high- and low-pressure explosion peninsulas as well as the individual first, second and third limits. The separate and coupled roles of H₂ and CO oxidation are identified, leading to enhanced insight of this foundational component in the mechanisms of hydrocarbon oxidation, as well as useful information in the utilization of syngas.

Keywords: syngas; explosion limits; eigenvalue analysis.

1. Introduction

The explosion limits of a given fuel/oxidizer mixture are the pressure-temperature boundaries of the mixture that separate regimes of explosion and non-explosion [1-3]. In particular, the explosion limits of H₂/O₂ mixtures, which exhibit a characteristic Z-shaped curve in the pressure-vs-temperature plot, with the three segments of this curve referred as the first, second and third limits, have been studied extensively [3-6]. Furthermore, it is well established that the first limit is controlled by the gas-phase chain branching reactions competing with radical diffusion to and deactivation at the wall; the second limit by the gas-phase H-O₂ branching and termination chain reactions; and the third limit by the gas-phase HO₂ and H₂O₂ chemistry competing with wall deactivation.

The corresponding explosion limits of H₂/CO/O₂ mixtures, whose chemistry not only represents the next level of complexity in fuels oxidation, beyond that of the H₂/O₂ chemistry, but it also forms the foundational block of hydrocarbon oxidation, have not been adequately explored. Fundamentally, while the oxidation of dry CO is an extremely slow process such that for all practical purposes it is considered to be un-ignitable, the addition of a minute amount of hydrogen, or a hydrogen-containing species, greatly promotes its reactivity in the role of a catalyst, and the term “catalyzing” has been used to describe this effect in the literature [7-9]. It is thus of interest to explore and quantify the extent of the catalytic effects in response to hydrogen addition, the state of the catalytic saturation with increasing addition, and the subsequent influence of the H₂ chemistry on the overall reactivity of the mixture, particularly in terms of the Z-shaped H₂/O₂ explosion responses. Such a study is also of obvious relevance to the recent interest in the combustion of syngas, which mainly consists of H₂ and CO, as it can be produced through gasification of coal and biomass and used in stationary gas turbines and IC engines [10, 11]. Furthermore, it is noted that reactions involved in syngas combustion play an essential role in the hierarchical structure of the oxidation models of hydrocarbon fuels [10].

Compared to hydrocarbons, the oxidation of CO/H₂ mixtures is governed by substantially smaller sizes in terms of the number of intermediate reactions and species. While such small size facilitates the simulation of CO/H₂ combustion, it nevertheless also renders the combustion response to be very sensitive to the individual reactions and species. Consequently, it is crucial for the reaction pathways to be clearly identified for the system.

In view of the above considerations, we shall simulate the explosion limits of H₂/CO/O₂ mixtures, with various amounts of H₂ addition, and identify the roles and limits of H₂ catalyticity and its subsequent dominance in terms of the Z-curve response at low and high concentrations, respectively. We shall further study the controlling chain branching and termination reactions as related to the separate and coupled chemistry of H₂ and CO oxidation, and derive explicit expressions for the various Z-shaped H₂/CO/O₂ explosion limits.

2. Computation Specification

The explosion limits of H₂/CO/O₂ mixtures were computed by the SENKIN code [12]. The explosion criterion at a given pressure and temperature is determined by 50 K increments at constant volume and adiabatic conditions. The calculation pressure range was from 3.5 to 3.2×10⁷ Pa, and the temperature range was from 300 to 2500 K. Based on uncertainty quantification and comparison of several recent syngas combustion mechanisms [13, 14], three chemical kinetic models with performance validations were employed in this study: namely the Kéromnès mechanism of 15 species and 49 reactions [15], the Davis mechanism of 14 species and 38 reactions [16], and the NUIG-NGM syngas sub-mechanism of 15 species and 41 reactions [17]. All the calculations were conducted for the stoichiometric concentrations. As found in previous studies, termination of radicals at wall has a strong effect on the explosion limits [6]. The carriers are destroyed at the wall with a temperature-dependent reaction as $R \xrightarrow{k_R} \text{wall}$ termination, where R denotes the radicals H, O, OH, HO₂, H₂O₂ and HCO in the system. The rate of wall termination [1] is given as $k_R = \frac{1}{4}\epsilon v \frac{S}{V}$, where ϵ is the efficiency of wall destruction, which is usually around 10⁻⁵ to 10⁻² for glass and quartz [2] and the value of $\epsilon = 10^{-3}$ is adopted; v is the average velocity of thermal motion of radicals; and S/V is the surface-to-volume ratio and for a spherical chamber S/V = 3/r. The radius of chamber is fixed as r = 37 mm in this study. As noted in [18], as the efficiency of wall destruction decreases, the effect of species diffusion decreases, and at the condition of $\epsilon = 10^{-3}$, the surface effect is controlled by the surface termination reaction. The percentage of hydrogen in the fuel mixture is defined as $F_{H_2} = C_{H_2}/(C_{H_2} + C_{CO})$, where C_i represents the mole concentration of species i .

3. Results and Discussion

3.1 Detailed solutions

Figure 1. Explosion limits of stoichiometric $\text{CO}/\text{H}_2/\text{O}_2$ with different kinetic mechanisms

The explosion limits of syngas, *i.e.* H₂/CO mixtures, with different H₂ mole fractions calculated with the three selected mechanisms are collectively shown in Figures 1 (a) and (b). In general, the results are qualitatively similar for the three mechanisms. Also, the deviations between the different mechanisms are much smaller for cases of high than low H₂ concentrations. The most severe deviations appear in the intermediate pressure range of 10³~10⁵ Pa.

The catalytic action of H₂ is demonstrated prominently in Figure 1 (b), which shows that while the explosion limit of pure CO is monotonic, it changes to Z-shaped with minute quantities of hydrogen addition, say with just 10⁻⁵ to 10⁻⁴ H₂ mole fraction in the fuel mixture for the surface deactivation reactions adopted. With further H₂ addition, the explosion limits move towards those of pure H₂.

Although the size of the detailed syngas mechanism is largely computationally accessible, availability of analytic formulas for the explosion limits can help to reveal the controlling parameters and chemical processes involved. The present investigation therefore aims to develop these formulas and provide accurate evaluations essentially equivalent to those found through computation with detailed chemistry. To further assist the analysis, the minimum kinetic reactions need to be identified in order to obtain concise analytical expressions. Consequently we have adopted the reduced mechanism of Boivin *et al.* [19], which includes 10 elementary reactions. Furthermore, the associated rate coefficients have been updated to the values of the Kromns mechanism. Furthermore, since the HO₂+H reactions, namely HO₂+H→H₂+O₂ and HO₂+H→2OH, as well as the HCO related reactions are only important for flame speed simulations, they are not included in the mechanism. The resulting 10-step reduced mechanism, consisting of eight H₂-O₂ related reactions (R1-R8) and two CO related reactions (R9 and R10), is listed as R1 to R10 in Table 1.

Figure 2. Comparison of explosion limits of syngas calculated by detailed mechanisms and the 10-step reduced mechanism (R1-R10 in Table 1)

Table 1. Reduced kinetic mechanism for CO/H₂/O₂ reaction system. Units: cm³-mol-s-cal-K, and $k = AT^n \exp(-E_a/RT)$

No.	Reaction	A	n	E_a
R1	$H+O_2 \xrightarrow{k_1} O+OH$	1.04E+14	0.00	15286.0
R2	$O+H_2 \xrightarrow{k_2} H+OH$	5.080E+04	2.67	6.292E+03
R3	$OH+H_2 \xrightarrow{k_3} H+H_2O$	4.38E+13	0.00	6990.0
R4	$H_2+O_2 \xrightarrow{k_4} H+HO_2$	5.176E+05	2.433	53502.0
R5	$HO_2+HO_2 \xrightarrow{k_5} O_2+H_2O_2$	1.300E+11	0.00	-1630.00
		3.658E+14	0.00	12000.00
R6	$H_2+HO_2 \xrightarrow{k_6} H_2O_2+H$	7.150E+4	2.54	21404.0
R7	$H_2O_2(+M) \xrightarrow{k_7} OH+OH(+M)$			
	$k_{7,\infty}$	2.00E+12	0.90	4.8749 E+04
	$k_{7,0}$	2.49E+24	-2.30	4.8749 E+04
R8	$H+O_2(+M) \xrightarrow{k_8} HO_2(+M)$			
	$k_{8,\infty}$	4.650E+12	0.440	0.00
	$k_{8,0}$	1.737E+19	-1.23	0.00
R9	$CO+OH \xrightarrow{k_9} CO_2+H$	7.015E+04	2.053	-355.67
		5.757E+12	-0.664	331.83
R10	$CO+HO_2 \xrightarrow{k_{10}} CO_2+OH$	1.570E+05	2.180	1.794E+04
R11	$CO+O(+M) \xrightarrow{k_{11}} CO_2(+M)$			
	$k_{11,\infty}$	1.362E+10	0.000	2384.00
	$k_{11,0}$	1.173E+24	-2.79	4191.00
R12	$CO+O_2 \xrightarrow{k_{12}} CO_2+O$	1.119E+12	0.000	47700.00

R7: Chaperon efficiencies are 3.7 for H₂, 6.0 for H₂O, 2.8 for CO, 1.6 for CO₂, 1.2 for O₂ and 1.0 for all other species. $F_{cent} = 0.43$.

R8: Chaperon efficiencies are 1.3 for H₂, 10.0 for H₂O, 1.9 for CO, 3.8 for CO₂ and 1.0 for all other species. $F_{cent} = 0.67$.

R11: Chaperon efficiencies are 2.0 for H₂, 12.0 for H₂O, 1.75 for CO, 3.6 for CO₂ and 1.0 for all other species.

Figure 2 compares the simulation results based on this simplified mechanism of R1 to R10 and the detailed mechanism. It is seen that when the hydrogen percentage in the fuel is larger than 10%, the reduced mechanism agrees well with the detailed mechanism. However, for cases with 5% and 1% H₂ in the fuel mixture, the reduced mechanism shows larger discrepancies with the detailed mechanism, especially at the second and third limits. Furthermore, while the detailed mechanism shows sensitive response of the second limit to changes of the fuel mixture, there is no such sensitivity for the reduced mechanism. To resolve such a discrepancy, we have added the following two reactions involving CO oxidation from the Kéromnès mechanism: R11: CO+O (+M)→CO₂ (+M) and R12: CO+O₂→CO₂+O, recognizing that they must be essential to the explosion limits of pure CO as they are the reactions without the presence of hydrogen.

Figure 3. Comparison of explosion limits of syngas (1% H₂) calculated by detailed mechanism and the reduced mechanisms (R1 to R12 in Table 1)

In Figure 3, the simulation results with this 12-step mechanism, namely the simplified mechanism R1 to R10 plus the additional R11 and R12 reactions, indeed agree well with those of the detailed simulation for the case of 1% H₂ in fuel. Specifically, the second limit shifts to lower pressures and higher temperatures by adding R11, demonstrating its importance in modifying the second limit at low X_{H2} conditions. Also, R12 is shown to be essential for the third limit. Consequently, we shall now identify this mechanism, summarized in Table 1, as the reduced mechanism.

Figure 4. Comparisons of explosion limits of syngas calculated by detailed mechanism and the 12-step reduced mechanism

Figure 4 then compares the explosion limits calculated by the detailed Kromns mechanism and the present reduced mechanism. It is seen that the explosion limits of syngas with different H_2 mole fractions are well represented by this reduced mechanism at various pressure, temperature and fuel compositions.

3.2. Eigenvalue analysis

To identify the controlling kinetics at various conditions, an eigenvalue analysis was conducted with the reduced mechanism, following the analysis of [6] for the pure H_2 system by neglecting the (very small) effects of heat release. Further, it is assumed that the concentrations of the reactants, H_2 , CO and O_2 , are orders of magnitude higher than those of the radicals, such as H and HO_2 , and hence the change of the reactant concentration is much smaller than its total concentration. This is reasonable because for such a thermodynamically closed system, the initial concentrations of the reactants are large compared to the maximum concentrations of the intermediates and the initiation step has a relatively small reaction rate. Then, the concentrations of reactants will not vary much over a reasonable time and can be treated as constants. Consequently, the reaction between a radical and a reactant is considered as quasi-first order and hence referred to as a linear reaction. On the other hand, a radical-radical reaction is intrinsically second order, which renders the system equations nonlinear. Since the radical concentrations are small compared with those of the reactants, effects of nonlinear reactions involving the collision of two radical molecules are unimportant in most cases. Nevertheless, they can moderately change the explosion limits at high pressures, which is mainly due to the radical-radical recombination, $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, as found in [4].

The pressure-dependent rates of R7, R8 and R11 have been incorporated into the analysis by using Troe's fitting [20] with F_c shown in Table 1. The third-body collision efficiencies of different species are included as well. Furthermore, to collapse the different collision efficiencies of different species and reactions into the reaction rate, the pressure-dependent reaction rate coefficients are written as $k_{i,eff} = k_i[M]_{eff}/[M]$, where $[M]_{eff}$ is the effective third-body concentration; the subscript *eff* of $k_{i,eff}$ is dropped hereafter to simplify the expressions. Consequently all the pressure-dependent rates can be expressed in term of $[M]$. For the $H_2/CO/O_2$ mixtures, we have $[M] = [H_2] + [CO] + [O_2]$. Assuming an ideal gas, the total gas concentration $[M]$ is proportional to the total pressure, that is $[M] = p/R^0T$. The linearized rate equations for the carriers H, O, OH, HO_2 and H_2O_2 are then given in matrix form as:

$$\frac{d}{dt} \begin{pmatrix} [H] \\ [O] \\ [OH] \\ [HO_2] \\ [H_2O_2] \end{pmatrix} = L \begin{pmatrix} [H] \\ [O] \\ [OH] \\ [HO_2] \\ [H_2O_2] \end{pmatrix} + \begin{pmatrix} I \\ J \\ 0 \\ I \\ 0 \end{pmatrix} \quad (1)$$

where $I = k_4 [H_2][O_2]$ and $J = k_{12} [CO][O_2]$ are the rates of the reactions $H_2 + O_2 \rightarrow H + HO_2$ and $CO + O_2 \rightarrow CO_2 + O$, respectively, and

$$L = \begin{bmatrix} -k_1[O_2] - k_8[O_2][M] - k_H & k_2[H_2] & k_3[H_2] + k_9[CO] & k_6[H_2] & 0 \\ k_1[O_2] & -k_2[H_2] - k_{11}[CO][M] - k_O & 0 & 0 & 0 \\ k_1[O_2] & k_2[H_2] & -k_3[H_2] - k_9[CO] - k_{OH} & k_{10}[CO] & 2k_7[M] \\ k_8[O_2][M] & 0 & 0 & -k_6[H_2] - k_{10}[CO] - k_{HO_2} & 0 \\ 0 & 0 & 0 & k_6[H_2] & -k_7[M] - k_{H_2O_2} \end{bmatrix} \quad (2)$$

With no radical in the initial mixture, there is a short initial period of slow radical generation through initiation reactions R4 and R11, which correspond to the terms I and J. This is followed by a stage of exponential radical growth, which is governed by the linearized matrix L. For this linearized system, if the real part of the eigenvalue of the coefficient matrix L is positive, then the intermediate concentrations of the corresponding eigenvector will increase exponentially with time, implying explosion. Otherwise, explosion fails. Consequently, the explosive limit is the boundary between the explosive and non-explosive regimes, for which the largest real part of the eigenvalues is zero.

Figure 5. Comparison of explosion limits of syngas calculated by simulations with detailed mechanism and eigenvalue analysis

Figure 5 compares the explosion limits given by simulation with the reduced mechanism and by prediction based on the reaction rate matrix. It is seen that the limits are close to each other except for high pressures and high H_2 concentrations at which the radical-radical reactions for the H_2 explosion become important, and for H_2 concentrations around 1% because of the progressive importance of heat release from the CO chemistry. It is also noted that, compared with the discrepancy among different mechanisms shown in Figure 1, the disagreements between analysis and detailed simulation are within the range of mechanism uncertainties. Consequently, although results from the eigenvalue analysis do not tightly match with the simulation results, analytical expressions for the explosion limits derived from such an analysis, to be presented in the sequel, are meaningful and of utility.

Figure 6. Sensitivities of wall termination rates of different chain carriers with (a) 5% H_2 and (b) 50% H_2 in fuel mixture

To further simplify the system, the sensitivities of the wall termination rates of different chain carriers were tested in Figure 6 for two typical fuel mixtures, with lower (5%) and higher (50%) H_2 concentrations, respectively. By modifying the wall termination rates to 10 times

larger or smaller than the original values, the response of the explosion limits curve shows at which condition the selected chain carrier is important. Moreover, since wall termination of the radicals is equivalent to the truncated time scales for the radicals, the quasi-steady states of the five carriers can be found by such an analysis. Results show that, similar to previous results on H_2/O_2 mixtures, the second limit is not sensitive to wall termination. On the other hand, the low-pressure first limit is sensitive to H termination and slightly sensitive to O termination at 5% H_2 condition (Figure 6a). The high-pressure third limit is sensitive to both HO_2 and H_2O_2 terminations. Specifically, the wall termination of HO_2 is essential for the upper turning from the second limit to the third limit, while the effect of H_2O_2 is more important at higher pressures. Based on these findings, the O and OH radicals can be assumed to be quasi-steady. Also, since the explosion limit responses are not sensitive to their wall terminations, surface destruction of O and OH can be neglected. Hence, their quasi-steady concentrations can be solved readily from Eqs. (1) and (2) as $[O]_{qss} = k_1[O_2][H]/(k_2[H_2] + k_{11}[CO][M])$ and $[OH]_{qss} = (k_1[O_2][H] + k_2[H_2][O]_{qss} + k_{10}[CO][HO_2] + 2k_7[M][H_2O_2])/(k_3[H_2] + k_9[CO])$. Consequently, the system is reduced from five to three variables.

To further facilitate interpretation, two parameters,

$$\alpha = \frac{k_2[H_2]}{k_2[H_2] + k_{11}[CO][M]} \quad (3)$$

$$\beta = \frac{k_6[H_2]}{k_6[H_2] + k_{10}[CO]} \quad (4)$$

are defined. Here, α is the fraction of the O radical going through reaction R2 as compared to the total amount in going through R2 and R11. Similarly, β is the fraction of the HO_2 radical going through reaction R6 as compared to the total amount in going through R6 and R10. As such, they respectively quantify the ratios of the O and HO_2 radicals reacting with H_2 as compared to the competing channels reacting with CO, and degenerate to unity for the pure H_2/O_2 system.

To understand how these two parameters affect the system response, the changes of α and β for three different conditions of pressure and temperature are shown in Figure 7. Specifically, Fig. 7(a) shows α and β over the entire range of the hydrogen percentage in fuel, which demonstrates that α has a sharp increase to unity at very small H_2 concentration, while β exhibits a smooth change from 0 to 1. To further expose the variation of α , Fig. 7(b) plots the growths of α and β in the catalytic regime (hydrogen percentage < 1%) on the log-log scale. It is seen that for the condition of 1000 K and 10^3 Pa, which is where the explosion limits curve shows dramatic changes in Fig. 1(b), the fast growth of α already starts at 10^{-5} to 10^{-4} H_2 in the fuel, while the slope is moderated beyond 10^{-3} H_2 in the fuel. This explains the finding in Fig. 1(b) that at 10^{-5} to 10^{-4} H_2 in the fuel the explosion limits become non-monotonic. Therefore, the fast transition from monotonic curve to Z-shaped curve corresponds to the high sensitivity of α . Finally, after α saturates to unity, the slow change of β is responsible for the subsequent mild explosion limit variation with H_2 addition.

Figure 7. Variations of the coefficients α and β with percentage of hydrogen in fuel at (a) entire concentration regime and (b) catalytic regime

With these two parameters, the governing equations for the three-variable system of $[H]$, $[HO_2]$ and $[H_2O_2]$ can be expressed as

$$\frac{d}{dt} \begin{pmatrix} [H] \\ [HO_2] \\ [H_2O_2] \end{pmatrix} = L_3 \begin{pmatrix} [H] \\ [HO_2] \\ [H_2O_2] \end{pmatrix} + \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} \quad (5)$$

where

$$L_3 = \begin{bmatrix} 2\alpha k_1[O_2] - k_8[O_2][M] - k_H & k_6[H_2]/\beta & 2k_7[M] \\ k_8[O_2][M] & -k_6[H_2]/\beta - k_{HO_2} & 0 \\ 0 & k_6[H_2] & -k_7[M] - k_{H_2O_2} \end{bmatrix} \quad (6)$$

Through eigenvalue analysis of equation (6), it is found that two eigenvalues of the three-variable system are always negative for the pressure and temperature ranges of interest such that a single eigenvalue determines the explosion limits. Consequently, the neutral condition between explosion and non-explosion can be derived explicitly from $\det(L_3) = 0$, yielding the following expression

$$F(T, P) = a[M]^4 + b[M]^3 + c[M]^2 + d[M] + e = 0 \quad (7)$$

$$a = 2f_{H_2}f_{O_2} \quad (8)$$

$$b = (2\frac{\alpha k_1}{\beta k_8}f_{H_2} - \frac{k_{HO_2}}{k_6})f_{O_2} \quad (9)$$

$$c = 2\alpha \frac{k_1}{k_8} \left(\frac{k_{HO_2}}{k_6} + \frac{k_{H_2O_2}}{\beta k_7}f_{H_2} \right) f_{O_2} - \frac{k_{HO_2}}{k_6} \frac{k_{H_2O_2}}{k_7}f_{O_2} - \frac{k_H}{\beta k_8}f_{H_2} \quad (10)$$

$$d = 2\alpha \frac{k_1}{k_8} \frac{k_{HO_2}}{k_6} \frac{k_{H_2O_2}}{k_7}f_{O_2} - \frac{k_{HO_2}}{k_6} \frac{k_H}{k_8} - \frac{k_{H_2O_2}}{k_7} \frac{k_H}{\beta k_8}f_{H_2} \quad (11)$$

$$e = -\frac{k_H}{k_8} \frac{k_{HO_2}}{k_6} \frac{k_{H_2O_2}}{k_7} \quad (12)$$

where $f_{H_2} = [H_2]/[M]$ and $f_{O_2} = [O_2]/[M]$.

Figure 8 compares the analytical results from the five- and three-variable analyses, showing that they agree well in most cases except for some slight differences at very low H_2 concentrations and very low pressures (below 10^3 Pa), which is mainly due to the quasi-steady assumption of O and OH. It is noted that although the three-variable analysis is slightly less accurate than the five-variable analysis, it still captures the key features of the explosion limits curves.

Figure 8. Comparison of explosion limits from 5- and 3-variable matrix analyses

3.3. The degenerate two-limit and single-limit expressions

From the above results, the low- and high-pressure limits can be readily assessed. For the low-pressure limit, since $k_6[H_2] \ll k_{HO2}$ and $k_7[M] \ll k_{H2O2}$, equation (6) yields a quadratic expression describing the lower peninsula of the explosion limits:

$$F_{LP}(T, P) = f_{O2}[M]^2 - 2\alpha \frac{k_1}{k_8} f_{O2}[M] + \frac{k_H}{k_8} = 0 \quad (13)$$

For the high-pressure situations, the H radical can be assumed to be in quasi-steady as Figure 6 shows that H radical termination is only important at low pressures. Consequently, the matrix L_3 is reduced to

$$L_{HP} = \begin{bmatrix} \frac{2\alpha k_1 k_6}{\beta} [H_2] - k_{HO2}(k_8[M] - 2\alpha k_1) & 2k_7 k_8 [M]^2 \\ k_6 [H_2] & -k_7 [M] - k_{H2O2} \end{bmatrix} \quad (14)$$

Based on the neutral condition that $\det(L_{HP}) = 0$, and also noting that $k_{HO2} \ll k_6[H_2]$ and $k_1 \ll k_8[M]$ at high pressures, the upper peninsula, for the high-pressure limits, is given by,

$$F_{HP}(T, P) = f_{H2}[M]^3 + \left(\frac{\alpha k_1}{\beta k_8} \frac{k_{H2O2}}{k_7} f_{H2} - \frac{k_{HO2}}{2k_6} \frac{k_{H2O2}}{k_7} \right) [M] + \alpha \frac{k_1}{k_8} \frac{k_{HO2}}{k_6} \frac{k_{H2O2}}{k_7} = 0 \quad (15)$$

From the above expressions for the upper and lower peninsulas, equations (13) and (15), the upper and lower turning points of the explosion limits curve can also be derived with the additional conditions that $\frac{\partial F_{LP}(T,P)}{\partial P} = 0$ and $\frac{\partial F_{HP}(T,P)}{\partial P} = 0$. The results of upper and lower parabola as well as the upper and lower turning points at different conditions are given in Figure 9.

Figure 9. (a) Low- and (b) high-pressure peninsulas and (a) lower and (b) upper turning points of the explosion limits

Furthermore, from equations (13) and (15), the three individual limits can also be readily identified. Specifically, the first limit is given by neglecting the second-order term in equation (13), as

$$2\alpha k_1[O_2] - k_H = 0 \quad (16)$$

while the second limit is given by neglecting the zeroth-order term, as

$$k_8[M] - 2\alpha k_1 = 0 \quad (17)$$

Similarly, from equation (15) the second limit is given by neglecting the third-order term, as

$$\left(\frac{\alpha}{\beta} k_1 k_6 f_{H_2} - k_{HO_2} k_8\right) [M] + 2\alpha k_1 k_{HO_2} = 0 \quad (18)$$

while the third limit is given by neglecting the last term,

$$[M]^2 + \left(\frac{\alpha k_1}{\beta k_8} \frac{k_{H_2O_2}}{k_7} - \frac{k_{HO_2}}{2k_6} \frac{k_{H_2O_2}}{k_7 f_{H_2}}\right) = 0 \quad (19)$$

It is noted that while both equations (17) and (18) are asymptotic expressions for the second limit, respectively approaching it from the low- and high-pressure peninsulas, equation (18) is more general by having the extra $\frac{\alpha}{\beta} k_1 k_6 f_{H_2}$ term to describe the effects of β as well as the HO_2 chemistry related to R6. As such, it is expected to be more accurate in describing the second limit, especially as it approaches the upper turning state.

Figure 10 shows that the three limits, given by equations (16-19), describe well the three branches of the complete limit curve, with equation (18) indeed provides a closer description of the second limit at higher pressures than equation (17). These results then clearly identify the influence of CO on the individual limits: the first limit is only affected by the parameter α characterizing the competition for the O radical, while the second and third limits are affected by the parameter β , which characterizes the competition for the HO_2 radical.

Figure 10. The (a) first, (b) second and (c) third asymptotic limits obtained by approximate quasi-steady-state analysis

4. Conclusions

In this study, the explosion limits of $\text{H}_2/\text{CO}/\text{O}_2$ mixtures were analyzed computationally and theoretically. It is shown that with minute quantities of hydrogen addition, about 10^{-5} to 10^{-4} in mole concentration for the present surface deactivation scheme, the explosion limits change from being monotonic to Z-shaped. Such dramatic change is explained by the highly sensitive variation of the kinetic parameter α , which characterizes the competition of O radical reacting with H_2 and CO. With further addition of H_2 , the explosion limits evolve towards those of the pure H_2 and become almost identical to it when the mole fraction exceeds 50%. This subsequent slow change of the Z-shaped curve is found to be controlled by β , which describes the competition of the HO_2 radical.

By applying eigenvalue analysis, the important kinetics and wall processes for the three limits are identified. The results show that for the low-pressure first limit, chain branching R1-R3 and the competing CO termination channel R11 and H wall termination are the controlling processes, while the surface destruction of the O radical is also important at low H_2 concentrations. The second limit is defined by the gas-phase reactions involved in both the kinetic parameters α and β . The HO_2 and H_2O_2 related gas-phase and surface reactions become important at higher pressures starting from the upper turning point, and H_2O_2 kinetics controls the third limit at very high pressures.

An explicit analytical expression for the explosion curve is derived, which can be further simplified by assuming quasi-steady states for the O and OH radicals. Based on this simplified result, explicit expressions are derived for the degenerate two-limit and single-limit states as well as the upper and lower turning points. All the analytical solutions provide concise yet accurate expressions for the explosion limits.

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