**Extinction limit and near-limit kinetics of lean premixed
stretched H₂-CO-air flames**

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Abstract

The extinction limit of laminar lean premixed stretched H₂-CO-air flames was investigated with particular attention to the chemical kinetic characteristics under near-limit conditions. The extinction stretch rates were determined by the digital particle image velocimetry measurement using the Counterflow Twin-Flame method. Corresponding numerical simulations were conducted using CHEMKIN II with detailed chemical kinetic mechanisms. The simulation results generally agreed well with the experimental data. It was found that increasing H₂ ratio restrained the flame from being extinguished, and this restraining effect was more profound low H₂ ratios. Further analyses of the flame speed, temperature and elementary reaction sensitivities revealed that H₂ addition played a crucial role in flame extinction by changing the competition between chain branching and termination reactions. To quantitatively measure the kinetic effect of H₂ addition, a dimensionless extinction exponent (β) defined as the ratio between the relative sensitivities of termination (ω_T) and branching (ω_B) reaction rates, i.e., $\beta = \partial \ln \omega_T / \partial \ln \omega_B$, was proposed. For a given syngas, β rapidly increased to a certain constant, defined as the critical extinction exponent, when the flame extinction was approached, despite variations in the stretch rate and changes in the loss mechanism. The chemical kinetic characteristics and loss mechanism jointly determined the extinction limit of lean premixed H₂-CO-air flames.

Keywords: chemical kinetics; extinction exponent; extinction stretch rate; lean premixed flame; synthesis gas.

53 **Nomenclature**

54 A_k , pre-exponential factor of the reaction rate coefficient of reaction k , c. g. s. unit system

55 Da , Damkohler number

56 $F_{\text{sen,R}}$, sensitivity coefficient of the extinction stretch rate to the chemical reaction rate

57 K , stretch rate, s^{-1}

58 K_{ext} , extinction stretch rate, s^{-1}

59 n_i , moles of species i , mole

60 p , pressure, atm

61 r , radial coordinate, cm

62 S_u^0 , laminar flame speed of an adiabatic 1-D free propagation flame, $\text{cm}\cdot\text{s}^{-1}$

63 $S_{u,\text{ext}}$, flame speed of a 1-D propagation flame under the extinction condition, $\text{cm}\cdot\text{s}^{-1}$

64 $S_{u,\text{ref}}$, reference flame speed of a stretched flame, $\text{cm}\cdot\text{s}^{-1}$

65 $S_{u,\text{ref,ext}}$, reference flame speed of a stretched flame under the extinction condition, $\text{cm}\cdot\text{s}^{-1}$

66 T , temperature, K

67 T_f , flame temperature, K

68 $T_{f,\text{ext}}$, flame temperature under the extinction condition, K

69 T_u , temperature of the unburned mixture, K

70 v , axis velocity, $\text{cm}\cdot\text{s}^{-1}$

71 y , axis coordinate, cm

72 α , H_2 ratio in the H_2 -CO mixture $\alpha = n_{\text{H}_2}/(n_{\text{H}_2} + n_{\text{CO}})$

73 β , extinction exponent

74 β_{ext} , critical extinction exponent

75 $\delta_{K_{\text{ext}}}$, experimental uncertainty of the extinction stretch rate, s^{-1}

76 δ_ϕ , experimental uncertainty of equivalence ratio

77 ϕ , equivalence ratio

78 ω_B , reaction rate of the branching reaction, $\text{mole}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$

79 ω_T , reaction rate of the termination reaction, $\text{mole}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$

80

81 **1. Introduction**

82 Synthesis gas (syngas) has recently attracted increasing interests due to its broad sources and
83 wide applications via direct combustion in gas engines or boilers for heat and power
84 generation. The main combustible components in syngas are H_2 and CO , as well as a small
85 amount of hydrocarbons with a considerable amount of dilutions such as CO_2 and N_2 . The
86 broadness of feedstock and variation in production technology result in diverse and complex
87 syngas compositions. Although the combustion mechanisms and flame behaviour of each fuel
88 component in its pure form in the syngas has been well studied and understood, those of the
89 mixtures with changing compositions are not insightfully understood and cannot be well
90 predicted because of the strongly synergetic effect between the combustion processes of H_2
91 and CO [1] as well as the effect of the diluents in the mixtures. Among the fundamental
92 characteristics, the extinction phenomenon and limits of syngas flames, which are of practical
93 significance to ensure the ignition quality, performance and safety of syngas-fired devices,
94 have become an active area in the combustion society.

95 For the premixed flames with single-component fuel, their extinction limits have been
96 extensively studied [2]. In particular, by employing the one-step reaction asymptotic
97 approach, Zeldovich [3] and Spalding [4] analytically proved that the extinction of a 1-D
98 planer flame subjected to volumetric heat loss is determined by competition between the heat
99 release and loss and there is an “extinction turning point” at which the laminar flame speed is
100 $e^{-1/2}$ times of its respective value under adiabatic condition. Law and Egolfopoulos [5, 6]
101 analysed the chemical kinetics on the flammability limits of the CHO -inert system and
102 revealed that both thermal loss and chain mechanism are crucial for the extinction of a

103 premixed flame subjected to only the intrinsic radiation heat loss. Accordingly, they
104 presented a unified chain-thermal theory and proposed a flammability exponent, the ratio of
105 the relative sensitivity of the termination reaction to that of the branching reaction, as a
106 criterion for the fundamental flammability limits [6]. This chain-thermal theory has been
107 applied to a number of numerical studies on the flame extinction (e.g., [7, 8]).

108 Besides radiation, the practical flame is usually subjected to other loss mechanisms, such as
109 naturally or artificially imposed aerodynamic stretch. For syngas flames, the complexity of
110 the fuel composition makes the extinction phenomena even more complicated. The chemical
111 kinetics of H₂ and CO are strongly coupled under near-limit conditions [9-14]. In particular,
112 increasing H₂ content provides more H and OH radicals which significantly accelerate the
113 reaction $\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$ [9, 14]. In addition, the flame stretch will induce a
114 preferential diffusion effect of H₂ and H to relocalise the key reactions [13, 15, 16], and
115 thereby remarkably affects the extinction phenomena. Dilution effects of N₂, CO₂ and H₂O
116 on the extinction and combustion of stretched H₂/CO flames have also been extensively

117 studied in the literature [11, 17-20] and the flames are believed to be weakened by the
118 combined thermal and chemical kinetic effect of the dilution [18]. A number of existing
119 studies [9-16, 18] indicated that the chemical kinetics indeed plays a crucial role in the flame
120 extinguishment, while none of them systematically and quantitatively studied the near-limit
121 chemical kinetic characteristics of H₂-CO-air flames. In addition, the existing experimental
122 studies [9-13, 15, 18] only covered a very limited range of H₂ ratios, α , (defined in a
123 customary manner $\alpha = n_{\text{H}_2}/(n_{\text{H}_2} + n_{\text{CO}})$, where n_{H_2} and n_{CO} denote the moles of H₂ and CO in
124 the syngas respectively), for example, 0.56 – 0.84 in [9], 0.13 - 0.50 in [15], 0.71 and 0.8 in
125 [13] and 0.10 in [18]. More experimental data covering a broader range of α under consistent
126 or comparable experimental conditions need to be collected to comprehensively study the
127 extinction limit of syngas of complex compositions.

In light of the aforementioned backdrop, the extinction of laminar, stretched, lean premixed syngas-air flames was experimentally and numerically studied over a wide range of H₂ ratios. In particular, the effect of varied chemical kinetics caused by the variation of fuel composition on the extinction of these flames was quantitatively assessed in the present study, seeking to shed new lights on the chemical kinetic characteristics in the syngas flame extinction phenomena.

2. Experimental

In order to minimise the disturbances by hydrocarbons and other impurities, and focus on the effect of H₂/CO ratio, the syngas fuels used in the present study were binary blends of pure H₂ (>99.99%) and CO (>99.5%). The H₂ ratio α varied over 0.02 – 0.9 (H₂/CO volumetric ratio from ~ 0.02 to 9.0). The oxidiser was compressed air, pre-dried through a silica-gel desiccator. The gas flow rates of H₂, CO and air streams were separately controlled by adjusting the upstream pressures of the sonic nozzle flow meters. The temperature and pressure of the unburned fresh gas mixtures were maintained at ambient conditions ($T_u = 298 \pm 3$ K and $p = 1$ atm).

The stretch rate (K) of a flame, namely the relative flame surface area variation, measures the mixture residence time in the flame zone [21]. A greater K indicates shorter residence time, and *vice versa*. As in the previous studies [2, 22], the extinction stretch rate (K_{ext}) was used to indicate the critical extinction state of a stretched H₂-CO-air flame. In the present study, K_{ext} was measured using the Counterflow Twin-Flame configuration in the state at which the flame was readily extinguished. As shown in Fig. 1a, the experimental system comprises two symmetrically-placed water-cooled burners with N₂ co-flow. The inner diameter of the burner exit and the distance between the two burners were both 10 mm. More detailed description and validation of this experimental system and the measurement accuracy using laminar flame speed data can be found elsewhere [18, 23]. Two flat twin flames were formed between

the two burners as shown in Fig. 1b. By gradually decreasing the fuel flow rate in the upstream, the unburned mixture became leaner and the twin flames moved towards each other and merged as a single flat flame until the extinction occurred. The axial flow velocity between the two nozzles was measured using a digital particle image velocimetry (DPIV). The local stretch rate K was determined as the absolute maximum velocity gradient along the axis (i.e., $K = |dv/dy|_{\max}$) in the hydrodynamic zone (upstream of points A and B in Fig. 1c) [9, 23]. The axial flow velocity at the edge of the preheat zone was defined as the reference flame speed ($S_{u,ref}$) [9, 23].

The experimental uncertainty for K_{ext} measurements (denoted by $\delta_{K_{ext}}$) was estimated following Moffat's method [24]. It combined the uncertainty of the DPIV measurement and that caused by the external disturbance (such as flow field disturbance and unburned gas temperature fluctuation). A detailed description of the measurement uncertainty analysis for $\delta_{K_{ext}}$ can be found elsewhere [18, 23]. In particular, the uncertainty of the DPIV measurements was estimated to be $< 3\%$. Thirty experimental runs were taken under each condition for K_{ext} measurements and the standard deviation of the thirty runs was calculated to indicate the uncertainty caused by external random disturbances. The confidence interval of the hereafter plotted error bars (in hereafter Figs. 2 and 3) was 95%. The uncertainty of ϕ (δ_ϕ) caused by uncertainties in the H_2 , CO and air flow rates could be estimated from the calibration data of the gas meters. Using the error transfer formula [24], δ_ϕ was estimated to be less than ± 0.008 .

3. Numerical Modelling

The Counterflow Twin-Flame configuration was simulated using the OPPDIF code originally developed by Kee and co-workers [25-27]. The code was modified to account for the thermal radiation of CO_2 , H_2O , CH_4 and CO in the optically thin limit [28], and integrated with the CHEMKIN II package and Sandia thermal and transport subroutines [29]. The equations

governing the Counterflow flame configuration included the continuity, energy conservation and species conservation derived from the Navier-Stokes equations in cylindrical coordinates. The temperature T and species mass fractions were assumed to vary along the flame axis y (shown in Fig. 1) only and pressure p was constant throughout the flow field. At the burner exit, the inlet velocity, temperature and species concentration were specified as the inlet boundary conditions. On the stagnation plane, the symmetry boundary condition was assumed to apply. The detailed mathematical derivation and explanation of the governing equations and boundary conditions can be found in Ref. [27].

Since H_2 has a strong mass diffusivity, a full multi-component diffusion coefficient formula was used in the computation with the thermal diffusion included as well. The governing equations were solved along a self-adaptive grid. The distance between the two burners was set as 10 mm, consistent with the experimental setup. The grid number was more than 800 (GRAD 0.02, CURV 0.05) so that the complex flame structure under the near-extinction condition was accurately captured. Similar to previous studies [30, 31], K_{ext} was computed using a one-point continuation approach that could realise the singular turning-point behaviour around the extinction state.

The detailed chemical kinetic mechanisms were used in the present study, and they included the widely-adopted ones proposed by Davis et al [32], Frassoldati et al [33] and Li et al [34, 35], thereafter referred as D-Mech, F-Mech and L-Mech, respectively. As shown in Fig. 1c, the computed central axial velocity profile well agreed with the experimental one. The computed K_{ext} was determined by the maximum gradient of the computed velocity profile in the hydrodynamic zone.

Sensitivity analysis was performed to evaluate the effect of each elementary reaction on K_{ext} . The sensitivity coefficient ($F_{\text{sen},R}$) of K_{ext} for each elementary reaction was determined according to Eq. (1)

$$F_{\text{sen,R}} = \frac{A_k}{K_{\text{ext}}} \frac{\partial K_{\text{ext}}}{\partial A_k} \quad (1)$$

where A_k denotes the pre-exponential factor of the rate constant of reaction k .

For comparison, the fundamental flammability limits of 1-D freely propagating flames subjected to only intrinsic thermal radiation loss were also computed using PREMIX code [25].

4. Results and Discussion

4.1 H_2 fraction effect on extinction limits of H_2 -CO-air flames

Firstly, the performances of the adopted kinetic mechanisms under extinction conditions of stretched H_2 -CO-air flames were compared and validated against the newly-obtained experimental data in Fig. 2. The computed K_{ext} 's using the three kinetic mechanisms all situated within the error bars of the experimental data when α was small (0.02, 0.1 and 0.3). However, the predictions with D-Mech and F-Mech exceeded the lower error bars, underestimating by 15% – 20 % when α was large (0.5, 0.7 and 0.9). Generally, L-Mech satisfactorily predicted the extinction limits for all tested cases. Thus, L-Mech was adopted in the hereafter analysis and kinetic studies.

Figure 2 also shows that the $K_{\text{ext}} \sim \phi$ curve was shifted left to the lower ϕ region as α increased, implying that the flame is less prone to be extinguished when α is larger. When the flame was equally stretched, ϕ at the extinction state (denoted as ϕ_{ext}) was significantly decreased by increasing α especially when α was low. The decrease in ϕ_{ext} was much more modest with increasing α when α was high. This result echoes the chemical kinetic studies of H_2 -CO-air flames [1]. Namely, a small amount of H_2 addition significantly accelerates CO oxidation while the acceleration is modest when H_2 content is high. The results indicate that the kinetic change caused by the variation of fuel composition is an important factor in determining the extinction state.

4.2 Flame speed and temperature under near-extinction conditions

As pointed out by Zeldovich [3] and Spalding [4], the competition between heat release and loss can be represented by the Damkohler number (Da) that is the ratio of characteristic flow residence time to reaction time. In the present stretched flame, the flow residence time was determined by the stretch rate K , and the reaction time was reflected by the flame speed. According to the asymptotic analysis using 1-step overall reaction assumption [3, 4], the flame speeds under the near-extinction conditions were expected to be approximately consistent if the flames were equally stretched. Figure 3a demonstrates that the flame speed at the extinction state ($S_{u,ref,ext}$) was roughly a function of K_{ext} , and large variation of fuel composition (α from 0.1 to 0.9, by 800%) only induced very limited change of $S_{u,ref,ext}$ (9% - 16%) when the flame was equally stretched. For instance, $S_{u,ref,ext}$ decreased by $\sim 13\%$, from $\sim 34 \text{ cm}\cdot\text{s}^{-1}$ to $\sim 30 \text{ cm}\cdot\text{s}^{-1}$, as α increased by 8 times from 0.1 to 0.9 at $K_{ext} = 600 \text{ s}^{-1}$. Considering the intrinsic limitation of the 1-step overall reaction assumption employed by Zeldovich and Spalding [3, 4], the disparity of $S_{u,ref,ext}$ (9% - 16%) should be reasonably ascribed to the detailed chemical kinetic change caused by the variation of the fuel composition.

To eliminate the stretch effect and focus on the kinetic and thermal effects, the singular extinction state of the 1-D freely propagating flame with only thermal radiation loss was computed using Law and Egolfopoulos's chain-thermal theory [5, 6]. Figure 3b compares the computed extinction flame speed $S_{u,ext}$ of 1-D flame using detailed kinetic modelling with its respective adiabatic flame speed S_u^0 using detailed kinetic modelling, as well as $e^{-1/2}S_u^0$ that is the estimated value of $S_{u,ext}$ using the 1-step overall reaction assumption as mentioned in the Introduction. $S_{u,ext}$'s estimated using the 1-step reaction assumption were 6% – 13% higher than those from detailed computation, confirming that ignoring detailed chemical kinetics may bring an error larger than 10% in determining the extinction state.

Figure 4 presents the variations of computed near-extinction flame temperatures ($T_{f,ext}$) with ϕ for the stretched H₂-CO-air flames. $T_{f,ext}$ increased with ϕ and was much more sensitive to ϕ rather than to K_{ext} . Thus, despite the wide variation in K_{ext} for the syngas flames with different fuel compositions, ϕ played a key role in determining the extinction. A smaller ϕ represents that the reactants are more diluted and the mole fraction of active radicals is lower. The results indicate that the radical chain branching and termination processes, as well as the flame temperature, are crucial for the flame extinction.

4.3 Near-limit kinetic analysis and the extinction exponent

The reaction rate sensitivity analysis on the extinction limit was further conducted for three cases in which their K_{ext} 's were approximately the same. The conditions of the three cases are listed in Table 1 and the sensitivity coefficients of the key reactions are shown in Fig. 5. The key reactions were CO + OH $\rightleftharpoons$ CO₂ + H (R1) and those H₂-O₂ reactions (R2-R11 in Fig. 5). Apart from the main fuel consumption reactions R1 and R4, K_{ext} was dominated by the chain branching reactions (e.g., R2, R3 and R5) and termination reactions (e.g., R9, R10 and R11).

It can be seen that H₂ played different roles at different α 's in the H₂/CO/air system. When α was small ($\alpha = 0.1$), R1 was the main fuel consumption reaction. Compared to CO, OH had a much lower concentration, becoming a major rate limiting factor of the entire reaction system. The reactions producing OH (R2, R3, R4 – R5) had large positive sensitivity coefficients and those consuming OH had negative sensitivity coefficients (R9, R10). H thus acted as a catalyst, being consumed by R2, R3 and R5, releasing OH, and then reproduced via R1. As α increased, the sensitivity coefficients of the reactions involving H increased rapidly. For instance, when $\alpha = 0.9$, the sensitivity pattern was quite similar to that of the H₂/O₂ combustion. OH was no long rate limiting anymore and R1 acted as a chain propagation reaction that passed the chain carrier from OH to H.

To quantitatively measure the competition between the branching and termination reactions, similar to the concept of the flammability exponent proposed by Law and Egolfopoulos [5], a dimensionless extinction exponent, β , was proposed to satisfy

$$\beta = \partial \ln \omega_T / \partial \ln \omega_B \quad (2)$$

where ω_B and ω_T are the reaction rates of the overall branching and termination reactions, respectively. To simplify the analysis, $\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$ (R2) and $\text{H} + \text{O}_2 + \text{M} \rightleftharpoons \text{HO}_2 + \text{M}$ (R11) were adopted as the key branching and termination reactions based on the sensitivity analysis to represent the overall ones. ω_B was represented by the maximum reaction rate of (R2), and ω_T was the rate of (R11) at the location of the maximum branching reaction (R2) rate.

From Eq. (1), β can be regarded as the ratio of the relative sensitivity of the termination reaction to that of branching reaction. A greater β indicates that the chemical process is more likely to be dominated by termination reactions, and *vice versa*. Figure 6 shows the variation of β with K . It is noteworthy that β rapidly increased as K approached K_{ext} , implying that the termination reaction became overwhelmingly dominant and consequently caused a rapid slowdown of the reaction. At the same time, T_f rapidly decreased as β rapidly increased until the extinction state was approached. As shown in Fig. 7, an approximately linear relation exists between $\ln \omega_{T,ext}$ and $\ln \omega_{B,ext}$ at a fixed α . This suggests that despite the wide variation of K_{ext} , β , equalling to the slope of the linear fitting line, approaches a constant value (denoted as β_{ext} , the critical extinction exponent, hereafter) at a given α . For instance, β_{ext} equals to 1.23, 1.04 and 0.99 when $\alpha = 0.1, 0.5$ and 0.9 , respectively. If these three β_{ext} values are incorporated in Fig. 6, the corresponding K 's at each respective β_{ext} are 506 s^{-1} , 547 s^{-1} and 446 s^{-1} , which are approximately identical to the K_{ext} values (518 s^{-1} , 540 s^{-1} and 456 s^{-1}) obtained from the detailed turning-point computation. This result provides an insight of the extinction limit by incorporating the loss mechanism and intrinsic chemical kinetics. When

the flame temperature is reduced to a certain value by either the change in stoichiometry or the increased flame stretch, the chain termination becomes dominant over the main branching reaction, inducing a further and rapid decrease of the flame temperature. Finally, the synergetic effect of the loss mechanism and chain termination results in the occurrence of flame extinction.

Figure 8 presents that the $\beta_{ext} \sim \alpha$ curve splits the whole domain into two regions, namely, combustible and incombustible. β_{ext} decreased with the increasing α and approached unity when α approached 1, agreeing with the flammability exponent of being unity for 1-D premixed H₂-air and CH₄-air flames [5, 6].

Though β and β_{ext} were used to describe the extinction of syngas, it is expected that this concept may well apply to other fuels, as long as key termination and branching reactions near the extinction could be well identified, such as the lean combustion of C₁ – C₄ alkane fuels [36, 37]. Verifications of the performance of β_{ext} for other fuels and flame extinctions induced by other loss mechanisms warrant further research.

5. Conclusions

The extinction limits of laminar lean premixed stretched H₂-CO-air flames were studied over a broad range of H₂/CO ratio. The experimental and numerical simulation results were in good agreement and both presented that H₂ addition significantly restrained the flames from being extinguished. Further analyses on the flame speed, temperature and elementary reaction sensitivities revealed that the H₂ addition greatly changed the competition between chain branching and termination reactions. A dimensionless extinction exponent was consequently proposed to quantitatively measure the competition between the chain branching and termination reactions. For a given fuel, the extinction exponent rapidly increased to a certain constant, defined as the critical extinction exponent, when the flame extinction occurred despite the broad variation in the local stretch rate and the change in loss mechanism. The

extinction limit of lean premixed H₂-CO-air flames was jointly determined by the loss mechanism induced by the flame stretch, radiation and the chemical kinetics at a given fuel composition.

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Figure Captions

Figure 1 Experimental approach: (a) schematics of the Counterflow flame burners (b) Counterflow flame image and (c) measured and computed flow velocity along the axis (L-Mech)

Figure 2 Experimental and computed extinction stretch rates (K_{ext}) of lean premixed stretched H₂-CO-air flames

Figure 3 Flame speeds of stretched (a) and 1-D free propagating (b) lean premixed H₂-CO-air flames under near-extinction conditions

Figure 4 Computed flame temperature in the extinction state as a function of the initial equivalence ratio of the mixture

Figure 5 Reaction rate sensitivity analyses on the extinction stretch rate (K_{ext}) of lean premixed H₂-CO-air flames

Figure 6 Variation of the extinction exponent (β) and flame temperature (T_f) as a function of the stretch rate (K)

Figure 7 Logarithmic plots of the net reaction rates of key branching and termination reactions for laminar premixed H₂-CO-air flames under near-extinction conditions

Figure 8 Critical extinction exponent (β_{ext}) of the lean premixed H₂-CO-air flame as a function of the H₂ ratio (α)

448 **Table captions**

449 Table 1 Description of the cases employed in the sensitivity analysis

450

451 Table 1 Description of the cases employed in the sensitivity analysis

	α	ϕ	$K_{ext} \text{ (s}^{-1}\text{)}$	$T_f \text{ (K)}$
Case1	0.1	0.438	343.8	1342.8
Case 2	0.5	0.282	344.6	1205.5
Case3	0.9	0.208	348.7	1149.6

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Figure 1

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