Chemical effects of hydrogen addition on soot formation in counterflow diffusion flames: Dependence on fuel type and oxidizer composition

Lei Xu\textsuperscript{a,b}, Fuwu Yan\textsuperscript{a,b}, Yu Wang\textsuperscript{a,b,*} and Suk Ho Chung\textsuperscript{c}

a. Hubei Key Laboratory of Advanced Technology for Automotive Components, School of Automotive Engineering, Wuhan University of Technology, Wuhan 430070, P.R. China
b. Hubei Collaborative Innovation Center for Automotive Components Technology, Wuhan 430070, P.R. China
c. Clean Combustion Research Center, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia

*Corresponding author:
Yu Wang
School of Automotive Engineering
Wuhan University of Technology
Wuhan, 430070, P.R. China
Email: yu.wang@whut.edu.cn

Full length article
Prepared for submission to Combustion and Flame
Chemical effects of hydrogen addition on soot formation in counterflow diffusion flames: Dependence on fuel type and oxidizer composition

Lei Xu\textsuperscript{a,b}, Fuwu Yan\textsuperscript{a,b}, Yu Wang\textsuperscript{a,b,*} and Suk Ho Chung\textsuperscript{c}

a. Hubei Key Laboratory of Advanced Technology for Automotive Components, School of Automotive Engineering, Wuhan University of Technology, Wuhan 430070, P.R. China
b. Hubei Collaborative Innovation Center for Automotive Components Technology, Wuhan 430070, P.R. China
c. Clean Combustion Research Center, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia

Abstract

We experimentally studied and kinetically modeled the effects of hydrogen addition on soot formation in methane and ethylene counterflow diffusion flames (CDFs). To isolate the chemical effects of hydrogen in such flames, we also ran a set of experiments on flames of the same base fuels but with the addition of helium. Specifically, we measured the soot volume fractions of the flames using the planar laser-induced incandescence technique. We simulated detailed sooting structures by coupling the gas-phase chemistry with the polycyclic aromatic hydrocarbon (PAH)-based soot model, using a sectional method to resolve the soot particle dynamics. Our experimental and numerical results show that hydrogen chemically inhibits soot formation in ethylene CDFs. While in methane flames, it is interesting to observe that the difference in soot production between the hydrogen- and helium-doped cases became much smaller when the oxygen concentration in the oxidizer stream ($X_O$) was reduced. This suggests that for methane CDFs the chemical soot-inhibiting effects of hydrogen was highly dependent on oxidizer composition (i.e., $X_O$). Explanations are provided through detailed kinetic analysis concerning the effects of hydrogen addition on the growth of PAH, soot inception, and soot surface growth processes. Our results suggest that hydrogen’s chemical role in soot formation not only depends on fuel type (ethylene or methane), it also may be sensitive to oxidizer composition.

Keywords: Hydrogen addition; soot; chemical effect; counterflow diffusion flame; soot modeling
1. Introduction

Effective strategies that control soot emissions from practical combustion devices are urgently needed to mitigate the adverse effects of soot particles on the environment [1] and human health [2-4]. The addition of non- or low-sooting tendency fuels in conventional hydrocarbons has long been regarded as a potential approach. Previous laboratory-scale studies demonstrated that the addition of hydrogen (H₂) could inhibit soot formation in shock tubes [5-8], laminar premixed flames [9, 10], coflow diffusion flames [11-17], as well as counterflow diffusion flames [18, 19]. The suppression of soot emissions through the addition of H₂ has also been reported under practical combustion conditions, such as in internal combustion engines [20-22] and turbulent non-premixed flames [23].

Despite these investigations, the underlying mechanisms of soot inhibition from the addition of H₂ are still not fully understood. Generally speaking, H₂ addition can influence soot formation through: 1) a dilution effect because H₂ reduces the carbon input; 2) a thermal effect due to the change in flame temperature from the addition of H₂; and 3) a chemical effect owing to the direct interaction of H₂ with flame and soot chemistry [12, 17]. In addition, in strained counterflow flames, preferential and differential diffusion also play important roles in the soot evolution processes [24]. Due to the distinctive role that H₂ plays in the growth of polycyclic aromatic hydrocarbon (PAH) [25, 26] and soot surface mass [27], the chemical effect of H₂ addition has been the focus of much research. The isolation of this chemical effect from other effects can be achieved by comparing the relative effectiveness of the addition of H₂ and He on the inhibition of soot formation [11, 13, 14, 16, 28]. Helium (He), as an inert gas, has similar thermal and transport properties as H₂ and consequently, the different soot-inhibiting effect between them is expected to be caused by the additional chemical effect of H₂. Computationally, fictitious H₂ (FH₂) (defined to have the same physical properties with H₂ but
does not participate chemical reactions) has also been used for the isolation of the chemical effect of the addition of \( \text{H}_2 \) \([10, 15]\).

A literature survey reveals that whether \( \text{H}_2 \) chemically promotes or inhibits soot formation in diffusion flames remains controversial. For instance, studies in ethylene/air coflow flames \([11, 16]\) indicated that hydrogen was more effective than He in inhibiting soot formation. The opposite was reported for methane coflow flames \([13, 29]\) in which the addition of \( \text{H}_2 \) was less effective than the addition of He in reducing soot formation, suggesting that \( \text{H}_2 \) may chemically enhance the production of soot. These results suggest the fuel-dependency of \( \text{H}_2 \)’s chemical effects on soot formation. In this regard, Liu et al. \([13]\) performed numerical simulations of both methane and ethylene coflow flames and successfully predicted the chemical promotive (inhibitive) effects of hydrogen on soot formation in methane (ethylene) flames. By comparing the numerical results with \( \text{H}_2 \) addition against that obtained with He addition, they further showed that the different chemical effects of \( \text{H}_2 \) were caused by its opposite effects on PAH growth and soot inception processes in methane and ethylene coflow flames.

The flow structures in coflow diffusion flames are rather complex. For instance, vortical structures have been observed near the nozzle region \([30]\), which may notably affect flow residence times along certain streamlines. The radial velocity profiles at the nozzle exit may differ significantly from the frequently assumed parabolic profile \([30]\) owing to nozzle heating \([31]\) and buoyancy effects, adding additional complexity to the specifications of boundary conditions. Small amounts of oxidizer can be entrained on the fuel side of coflow flames through the stabilizing quenching zone at the flame’s base (due to excessive heat and radical losses to the nozzle) \([32]\). These complications, together with the multi-dimensional nature make detailed kinetic analysis of the chemical effect of \( \text{H}_2 \) addition in coflow
flames unnecessarily challenging. An alternative would be to employ a quasi-one-dimensional counterflow diffusion flame (CDF). Due primarily to its simpler flow field and relative ease of modeling, CDF is particularly suitable for studying the fundamental chemistry of soot evolution [33-36], e.g., the fuel mixing effects on soot formation [37, 38] as performed in this work. Additional benefits of CDF include its relevance to the laminar flamelet model [39], its resistance to buoyancy-driven instability especially under high-pressure conditions [40], its capability to provide a sooting zone without interference from soot oxidation [41, 42]. The quasi-one-dimension feature also means different soot processes may dominate at different axial positions and analysis of such processes is considerably easier because they would not be convoluted by different processes along the radial direction, as will likely happen in other multi-dimensional flames. In a CDF, there typically exists a region where abundant nascent small particles exist from inception, but soot volume fraction is relatively small. Therefore, the investigation on the soot inception process may be highlighted in this region, not to be influenced by the much higher soot concentration in the downstream soot growth region [43].

To the best of our knowledge, only two studies have focused on the chemical effects of the addition of H\textsubscript{2} on soot formation in CDFs [18, 28] (a third study by Choi et al. [19] using transmission electron microscopy reported the overall effect of H\textsubscript{2} addition to decrease soot sizes while enhancing the formation of fullerene nanostructures). Du et al. [18] experimentally observed that H\textsubscript{2} addition can decrease soot inception limit in ethylene CDFs, but less effective than He addition. However, without detailed kinetic modeling, this study remained inconclusive as to the exact process by which H\textsubscript{2} suppresses soot inception. A modeling study by Guo et al. [28] showed that H\textsubscript{2} addition in ethylene CDFs has stronger soot-inhibiting effects and led to lower soot volume fractions than He addition.
Given that the work of Du et al. [18] is a purely experimental study primarily focused on initial soot inception whereas that of Guo et al. [28] is a purely numerical study and that the two studies present somewhat opposing views, we believe that it is of interests to clarify, through combined efforts of experiments and detailed soot modeling, how H\(_2\) addition chemically affects soot formation in ethylene CDFs. This may be especially important considering the fact that so far no quantitative soot volume fraction measurements have yet been conducted on CDFs with H\(_2\) or He addition.

A second motivation of this work is to confirm whether the fuel dependence of the chemical effect of H\(_2\), as observed in coflow diffusion flames, is also present in CDFs. As a matter of fact, there is no previous studies on the effects of hydrogen addition in methane CDF. Indeed, as will be detailed later, the experimental data and numerical predictions of the present work showed that H\(_2\) addition is more effective than He in reducing soot formation in ethylene CDFs. While for methane flames, it will be shown for the first time that the relative effectiveness of H\(_2\) and He addition in reducing soot formation can be highly dependent on oxygen mole fraction in the oxidizer stream. Explanations for these interesting phenomena are provided based on detailed kinetic analysis of the numerical results.

Specifically, axial profiles of soot volume fractions in H\(_2\)/He doped ethylene and methane CDFs were quantitatively measured in this work with the laser-induced incandescence (LII) techniques. Soot modeling were performed by coupling a detailed gas-phase chemistry and a recently proposed PAH-based soot model. In subsequent sections, the experimental apparatus and numerical methods are firstly introduced. Measured data are then presented and compared with numerical predictions. Finally, detailed kinetic pathways were discussed to elucidate the possible mechanisms of the effects of H\(_2\)/He addition in ethylene and methane flames. The dependence of these effects on fuel type and oxidizer composition are also highlighted.
2. Experiment

The experimental apparatus is similar to one previously described [44, 45], consisting of a counterflow burner, a flow control system, and a laser-based measurement setup. The burner had two opposing contoured nozzles with 10 mm i.d. and a separation distance (L) of 8 mm. The fuel and oxidizer streams were maintained at ambient temperature and introduced from the lower and upper nozzles, respectively. Annular slits surrounding both nozzles provided nitrogen shields to avoid disturbance from the ambient air. The base fuels used were methane and ethylene, and H$_2$ was added to the fuel stream (all fuels are CP grade). In an effort to isolate the chemical effect of H$_2$, contrasting experiments using He as a fuel additive were also performed. The oxidizer was composed of oxygen and nitrogen with the molar fraction of oxygen, $X_O$, being 0.24 or 0.45, depending on the individual flame. All the flow rates were controlled by thermally-based mass flow controllers.

Soot volume fractions (SVFs) were quantified using a laser-induced incandescence (LII) technique [46-48]. The fundamental emission (1064 nm) of an Nd-YAG laser was manipulated to form a laser sheet 8 mm height at the center of the burner. The LII signals, after passing a narrow-band filter at 400 nm (40 nm FWHM) were detected by an intensified CCD camera with zero gate delay and a gate width of 80 ns. The LII signals were averaged from 600 laser shots to reduce noise. The measurement uncertainty was estimated from the standard deviation to be less than 5%.

Additional light extinction (LE) measurements [49] with a near-infrared laser beam at the wavelength of $\lambda = 980$ nm were made to calibrate the LII signals. The choice of infrared beam was based on the fact that light in the visible spectrum is likely to be absorbed by gaseous PAH species as well as by soot particles [50-52]. A tomographic inversion was performed to convert the line-of-sight extinction coefficients to local values [53]. In our setup, the calibration factor was determined to be
10,000 LII signal counts corresponding to an SVF of 0.363 ppm. More details concerning the LE setup are presented in our previous study [54].

3. Numerical modeling

Simulations of soot formation were conducted by coupling a detailed gas-phase mechanism [55] with a PAH-based soot model [56]. The gas-phase mechanism was based on AramcoMech 1.3 [57] with an extension to account for benzene formation [58] and PAH growth up to coronene [59, 60]. The details of the soot model were previously described [56] and thus only a brief description is given here.

Eight PAH species with sizes ranging from pyrene to coronene were allowed for the inception of nascent particles through either homogeneous or heterogeneous nucleation. The nucleation reactions (total 36) are assumed to be irreversible with zero activation energy, and nucleation rates were calculated based on the size-dependent collision efficiency, \( C_E \) [61]. In particular, if the two colliding PAH species are the same, the nucleation rate can be expressed as [56]:

\[
R_c = \gamma \times C_E \times E_F \times \sqrt{\frac{4\pi k_B T}{m_i}} \times \frac{N_d^2}{N_{a}^2} \times \frac{C_i^2}{D_i^2}
\]

Where \( m_i \) and \( D_i \) is the mass and the collision diameter of the \( i \)th PAH molecule, respectively, \( C_i \) is the concentration. \( E_F \) is the van der Waals enhancement factor of 2.2, and \( \gamma \) is a correction constant which is introduced to match with the soot volume fractions of the target ethylene and methane flames.

Note that the present soot nucleation sub-model has certain assumptions (i.e., irreversible physical dimerization of large PAHs) that may not represent a complete description of the actual physicochemical pathways leading to soot inception. In fact, soot nucleation remains the least-known process of soot formation. The physical dimerization of PAH is widely used in existing models; however, it has limitations in explaining the stability of PAH dimers bonded by van de Waals interaction forces at high
flame temperature [2]. It is possible that chemical bonds can be formed between PAHs [4, 62], although the purely H-abstraction based chemical coagulation mechanism also has limitations in accounting for rapid soot nucleation in regions with limited reactive H radicals [2].

Recently, new nucleation pathways have been proposed. For instance, Johansson et al. [63] recently proposed the CHRCR (clustering of hydrocarbons by radical-chain reactions) mechanism to explain the fast molecular growth and the formation of covalently-bonded large molecular clusters (incipient particles). Violi and coworkers [64, 65] reported that the aliphatic chains attached to aromatic rings may favor the physical sticking of PAHs (into clusters) at high temperatures. Eaves et al. [66] noted reversibility may be important in physical PAH dimerization. In addition, Kraft and coworkers [67, 68] showed that curved PAHs can bind strongly with chem-ions and thus could be an important mechanism in soot nucleation. Similar ion-induced nucleation was also suggested by Carbone et al. in an effort to explain the unexpected high soot growth rate in low temperature region of premixed [69] and non-premixed flames [70, 71]. It is possible that many mechanism (such as physical dimerization, chemical growth, aliphatic chains, ion-induced and RSR-propagated mechanism) can simultaneously contribute to nucleation. Nevertheless, detailed rates for reactions that are involved in these nucleation mechanisms are still unavailable for incorporation into numerical models. Therefore, for a quantitative prediction of soot formation, many existing soot inception models are typically developed based on the dimerization of different-sized PAHs [72-75]. In particular, the present work utilized the well-established models based on dimerization of large PAHs (4 rings and larger), which has been used widely by various research groups [34, 76, 77] and successful in explaining many experimental observations. We nevertheless note more work needs to be done to improve the model to account for most recent fundamental development in soot inception mechanisms.
Soot surface mass growth is described by the modified surface hydrogen-abstraction-\(\text{C}_2\text{H}_2\)-addition (surface HACA) mechanism [78] with the addition of \(\text{C}_2\text{H}\), \(\text{CH}_3\), and \(\text{C}_3\text{H}_3\) as reactants in the hydrogen abstraction reactions [56]. Addition of PAHs on the surface of particles was assumed to be an irreversible physical process with zero activation energy. Note, although several studies have attempted to introduced the reversibility in modeling the PAH addition processes [66, 79, 80], however, rate parameters were still not fully established for many PAHs involved in the present model. Therefore, the addition of PAH was modelled as an irreversible process for simplicity, an assumption that has also been adopted by other researchers [15, 77] to explain, for examples, the effects of \(\text{CO}_2\) addition on soot formation. Particle coagulation was assumed to occur in the free-molecular regime with a collision efficiency of 2.2 (after multiplying the van der Waals enhancement factor) [81]. Soot oxidation by OH radicals was described by a constant collision efficiency of 0.13 [78] while soot oxidation with \(\text{O}_2\) was based on the oxidation of pyrene proposed recently by Celnik et al. [82].

Similar to our previous work [83], we used a discrete sectional method [62, 80, 84] to resolve the particle size distribution (PSD). Compared to the method of moments which gives only statistical information (moments) about the size distribution, the sectional method has an advantage of being able to resolve the PSD itself (although with limited resolution). The whole soot particle mass/volume range was discretized into 25 sections. Within each section, all primary soot particles were assumed to be spherical with a density of 1.8 g/cm\(^3\) [85]. The first section was modeled with a representative size of 0.878 nm, corresponding to the smallest particle in the model, i.e., a dimer of pyrene (\(\text{C}_{16}\text{H}_{10}\)). With a spacing factor of 2 (i.e., the mass/volume ratio of two consecutive sections), the sectional representative sizes in the range of 0.878–224.8 nm were covered. We confirmed that the computed soot properties remained unchanged with further increases in the section numbers.
Individual species diffusion velocity was determined using a mixture-averaged formulation given in [86]. Thermal diffusion velocities of light molecular species (H₂, He and H) and particle thermophoresis effects [87] were taken into account. Radiation heat loss through CO₂, CH₄, CO, and H₂O as well as soot was included in the energy equations by using an optically thin approximation (i.e., neglecting self-absorption of radiation) [88, 89]. The gas-phase and particle-phase transport equations were solved in a segregated manner with iteration until convergence, using the opposed-flow module in the Chemkin package [90].

4. Results and discussion

In this section, we first report experimental data on the effects of H₂ or He addition on soot formation in ethylene and methane CDFs, which were summarized in Table 1. Then, we present kinetic analyses based on the numerical results from a soot model, attempting to discern the possible causes of the observed effects of H₂ or He addition on soot formation.

In the ethylene CDFs, the oxidizer stream was composed of 24% oxygen and 76% nitrogen (i.e., the molar fraction of oxygen, $X_O$, was 0.24) and the fuel stream was ethylene with the addition of up to 30% H₂ or He ($X_{H₂}/X_{He}$). In the methane CDFs, $X_O$ was 0.45 and up to 20% $X_{H₂}$ or $X_{He}$ was added. We used the higher value of $X_O$ in methane flames to achieve a moderately sooting flame for accurate SVF quantification. Similar strategies were used by Glassman and coworkers when they were studying fuels with significantly different sooting tendencies [32]. The nozzle exit velocities for all cases were maintained at $V = 13.5$ cm/s. We realized that the addition of H₂ or He would lead to a minor change in strain rate, $a$ (defined as $a = \frac{2V_O}{L} \left(1 + \frac{V_F\sqrt{\rho_F}}{V_O\sqrt{\rho_O}}\right)$ [91, 92]) by varying the fuel stream density, $\rho_F$. The impacts of on this change on the residence time and thus on the relative soot production of H₂- and
He-doped flames was found to be negligible.

Table 1. Flow rate conditions and the corresponding LII data for target flames.

<table>
<thead>
<tr>
<th>H2/He (in mol)</th>
<th>Fuel</th>
<th>H2/He (L/min)</th>
<th>O2</th>
<th>N2</th>
<th>Peak ( f_v ) (10^7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2H4 as fuel, ( X_0 = 0.24 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( X = 0 )</td>
<td>0.636</td>
<td>0</td>
<td>0.153</td>
<td>0.483</td>
<td>5.12 (5.12)</td>
</tr>
<tr>
<td>( X = 0.05 )</td>
<td>0.604</td>
<td>0.032</td>
<td>0.153</td>
<td>0.483</td>
<td>4.10 (4.51)</td>
</tr>
<tr>
<td>( X_0 = 0.1 )</td>
<td>0.572</td>
<td>0.064</td>
<td>0.153</td>
<td>0.483</td>
<td>3.20 (3.94)</td>
</tr>
<tr>
<td>( X_0 = 0.15 )</td>
<td>0.541</td>
<td>0.095</td>
<td>0.153</td>
<td>0.483</td>
<td>2.24 (3.30)</td>
</tr>
<tr>
<td>( X_0 = 0.2 )</td>
<td>0.509</td>
<td>0.127</td>
<td>0.153</td>
<td>0.483</td>
<td>1.55 (2.76)</td>
</tr>
<tr>
<td>( X_0 = 0.25 )</td>
<td>0.477</td>
<td>0.159</td>
<td>0.153</td>
<td>0.483</td>
<td>0.978 (2.26)</td>
</tr>
<tr>
<td>( X_0 = 0.3 )</td>
<td>0.445</td>
<td>0.191</td>
<td>0.153</td>
<td>0.483</td>
<td>0.592 (1.70)</td>
</tr>
<tr>
<td>CH4 as fuel, ( X_0 = 0.45 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( X = 0 )</td>
<td>0.636</td>
<td>0</td>
<td>0.286</td>
<td>0.350</td>
<td>0.885 (0.833)</td>
</tr>
<tr>
<td>( X = 0.05 )</td>
<td>0.604</td>
<td>0.032</td>
<td>0.286</td>
<td>0.350</td>
<td>0.604 (0.760)</td>
</tr>
<tr>
<td>( X = 0.1 )</td>
<td>0.572</td>
<td>0.064</td>
<td>0.286</td>
<td>0.350</td>
<td>0.394 (0.663)</td>
</tr>
<tr>
<td>( X = 0.15 )</td>
<td>0.541</td>
<td>0.095</td>
<td>0.286</td>
<td>0.350</td>
<td>0.237 (0.596)</td>
</tr>
<tr>
<td>( X = 0.2 )</td>
<td>0.509</td>
<td>0.127</td>
<td>0.286</td>
<td>0.350</td>
<td>0.135 (0.527)</td>
</tr>
</tbody>
</table>

4.1 Overall flame and sooting structure

The flames we investigated were all soot formation (SF) flames [42]. Their reaction zones were on the oxidizer side of the stagnation plane, such that newly incepted soot would be convected away from the flame and towards the stagnation plane. During this process, soot particles continued to grow via surface HACA growth along with coagulation, while oxidation was largely absent. The choice of studying the effects of the addition of H2 in SF flames allows us to concentrate on soot inception and soot surface growth processes without interference from soot oxidation.

A presentation of the overall sooting structure is helpful for understanding the soot evolution processes in the CDFs studied here. In this regard, we show in Fig. 1 the computed profiles of temperature and important intermediate species (a), the mole fractions of aromatic species (b), soot number density and average diameters (c), and soot volume fractions (d) as a function of the distance.
from the fuel nozzle, $z$, for a representative H$_2$-doped C$_2$H$_4$ flame with $X_{\text{H}_2} = 0.2$.

Fuel pyrolysis products such as C$_2$H$_2$ and C$_3$H$_3$ (a) are located on the fuel side of the flame sheet (represented by the location of the maximum flame temperature, $z_{T,\text{max}}$), where PAH species (A1-A4) are also abundant (b). Here, A stands for aromatic ring and A1, A2, and A4 are benzene, naphthalene, and pyrene, respectively. Nascent soot particles are incepted from large PAHs on the fuel side, where abundant soot particles exist (c). After their inception, soot particles are transported via convection towards the particle stagnation plane, $z_{\text{st,p}}$ (the gas-phase stagnation plane is marked as $z_{\text{st,g}}$), crossing a region where oxidizing species such as OH and O$_2$ barely exist. Soot particles will therefore grow in mass and size while their destructive oxidation is limited during this convection process.

Along the direction of convection, both the soot diameter, $D_{63}$ (c) and SVF (d) continues to increase and reaches a peak value near $z_{\text{st,p}}$. The drop in SVF or soot diameter across $z_{\text{st,p}}$ occurs because the particles have very low diffusivity and eventually leak out radially. As a result, the experimental profile of SVF (and soot diameter) exhibits a skewed shape, which was also reproduced by the soot model. During this process, the soot number density ($N_s$) drops continually. Note the experimental data of soot diameter and soot number density were obtained by performing additional light extinction/scattering measurements, during which a He-Ne laser with a wavelength of 632.8 nm was used as the light source. Details concerning the experimental setup are presented in our previous study [54]. The data reduction procedure was the same with that employed in Ref. [56]. Notice that the predicted number density is higher than the measured result. This may be partly because in deriving $N_s$, an assumption of self-similar particle size distribution was made [56]. In reality, however, the size distribution could be varying with $z$. Furthermore, it is highly likely that the present experimental technique (extinction and scattering) is not effective in detecting nascent small particles which contribute negligibly to soot
volume fraction but account for a considerable portion of number density. Such ineffectiveness is believed to be caused by the significantly different optical properties of nascent particles as compared to those of mature particles. In fact, there are studies that suggest nascent soot particles can be liquid-like and transparent [2].

![Diagram showing computed flame and sooting structures of H₂-doped ethylene counterflow diffusion flames (X₀= 0.24, X₉H₂=0.2) along with measured soot volume fraction (circular symbols), soot diameter (square) and number density (triangle). The measured profiles are shifted by 0.2 mm towards the oxidizer side to account for the potential buoyancy effect.](image)

**Fig. 1.** Computed flame and sooting structures of H₂-doped ethylene counterflow diffusion flames (X₀= 0.24, X₉H₂=0.2) along with measured soot volume fraction (circular symbols), soot diameter (square) and number density (triangle). The measured profiles are shifted by 0.2 mm towards the oxidizer side to account for the potential buoyancy effect.

This explanation may be also supported by the fact that there was almost no scattering signal on the fuel side of the stagnation plane (z = 1.5–2.4 mm) although the predicted soot number density is significant, as shown in **Fig. 1(c)**. This is consistent with observations by D’Anna and coworkers [41,
93] in an ethylene SF flame and can be attributed to the physical collision between PAHs leading to the formation of soot nuclei, given that relatively high mole fractions of PAH molecules are still present in this region. However, due to the low flame temperature (<1000 K), the mass growth of soot via the surface HACA mechanism is inhibited in this region. Consequently, the newly incepted particles barely grow as they are transported toward the location of \( z_{\text{st,g}} \), leading to their small average sizes and their weak contribution to the soot volume fraction.

The reasonable agreements between the predictions and experiments in terms of the profiles of soot diameter and soot volume fraction suggest that our model is capable to resolve the major feature of the soot evolution process in the present CDFs. Moreover, the quantitative variation of soot concentration of various H\(_2\)- and He- doped flames, which is the primary research objective of this work, is reasonably captured by the present soot model. In this regard, it is our opinion that the soot model is acceptable for the present analysis.

4.2 Effects of H\(_2\)/He addition: Experimental and numerical data

To elucidate the effects of the addition of H\(_2\) on soot formation quantitatively, we plotted the normalized experimental and simulated peak SVFs of ethylene CDFs with various H\(_2\)/He doping ratios in Fig. 2. It has been confirmed that the variation of peak SVFs is qualitatively similar to that of the integrated values, i.e., the total soot loadings in the whole flame region. The experimental data show appreciable decreases in SVF as \( X_{\text{H}_2} \) or \( X_{\text{He}} \) increases. Moreover, the addition of H\(_2\) was found to be more effective in reducing soot formation than was the addition of He, which was well reproduced by the simulation. On the other hand, both the experiments and predictions in Fig. 3 showed that H\(_2\) or He addition reduced soot particle sizes. Furthermore, H\(_2\) addition was found to be more effective in
reducing soot diameter than He. These results suggest that the present soot model can capture the underlying effects of H₂ or He on soot formation process. Note the calculated maximum flame temperature in the H₂ addition case is higher than that in He addition case at a same $X$, the primary reason being the preferential diffusion of H₂ [94, 95].

**Fig. 2.** Effects of H₂/He addition on the peak $f_\nu$ in ethylene counterflow diffusion flames (data normalized to of peak SVF of a neat ethylene flame).

**Fig. 3** The computed and measured soot diameter profiles for neat C₂H₄ and H₂/He-doped flame. The measured profiles are shifted by 0.2 mm towards the oxidizer side.

Since He is chemically inert, the reduction in SVF with the addition of He can occur from both thermal (reduction in flame temperature) and dilution (reduction in fuel concentration) effects. Moreover, the preferential diffusion effects of He [20] may also decrease the formation of soot in
strained CDFs. Since preferential diffusion of He takes effect mainly through modifying local concentrations of soot precursors in the soot formation region, we artificially define it as part of the dilution effects.

H₂ has specific heat and transport properties similar to those of He. Its thermal and dilution effects on the formation of soot are expected to be quantitatively similar to the case when He is added. The observed greater reduction in soot formation with the addition of H₂ can be attributed to a chemical effect from H₂, either via an increase in the flame temperature from additional heat release (including preferential diffusion) or via directly participating in the soot formation chemistry. The detailed chemical effects of H₂ on soot formation will be elaborated in a later section by comparing against the case of He addition, following the approach employed in several previous studies [11, 28].

In methane flames with \( X_O = 0.45 \), the soot model was validated against the SVF profile for the neat methane flame (Fig. 4a). Experimental and simulation results both show monotonic decreases in peak SVFs as \( X_{H_2}/X_{He} \) increases (Fig. 4b). Interestingly, the effect of the addition of H₂ on reducing soot formation is more pronounced than that of He, which is similar to the ethylene case. Note again that, although we have tuned the soot inception rate (by adjusting a correction constant \( \gamma \) [56]) to match the maximum SVF of the neat methane flame, that parameter is then fixed and maintained unchanged for the H₂ and He addition cases. Quantitatively, the experimental results show that the addition of H₂ leads to an even more significant chemical suppression of soot formation in methane flames than in ethylene flames. For instance, adding 20% H₂ to the methane CDF led to a 46% lower SVF than did the addition of He, whereas in ethylene CDF, the reduction was only 14%. These results are in contrast to previous data reported for coflow methane/air flames (\( X_O = 0.21 \)) [13, 29], which indicated that the addition of He was more effective than the addition of H₂ in inhibiting soot formation in methane-air
coflow flames and suggested the chemically promoting effects of H$_2$.

![Graph of soot volume fraction profile](image1.png)

**Fig. 4.** (a) Computed soot volume fraction profile against LII data (symbol) for neat CH$_4$ flame and (b) Computed and experimental normalized maximum $f_v$ for various H$_2$/He doped CH$_4$ flame ($X_O = 0.45$).

These discrepancies certainly deserve further investigation. However, since we used a much higher $X_O$ of 0.45 to achieve moderately sooting CH$_4$ CDFs in our experiments, we needed to verify if the differing chemical effects of the addition of H$_2$ in methane CDF and in coflow diffusion flames is an indication of configuration-based differences or if these effects were merely a result of the different $X_O$ conditions. In this regard and in an effort to identify the potential effects of oxygen content ($X_O$) on the chemical effect of H$_2$, we tried to assess the soot loading of the methane flame with at $X_O = 0.24$ (similar to the composition of the oxidizer we used in the C$_2$H$_4$ flames) with light scattering measurement. However, we could not get confident data due to its rather low level of soot loading. As a result, for measurement purposes, we increased $X_O$ from 0.24 to 0.30 (hence higher soot loading) and compared experimentally the effects of H$_2$/He on soot scattering intensities in methane flames between
the $X_0 = 0.45$ and $X_0 = 0.3$ cases.

The experimental results are given in Fig. 5a, confirming that the chemical effect of H$_2$ addition on reducing soot formation was largely reduced as $X_0$ decreased from $X_0 = 0.45$ to 0.3. Quantitatively, 10% H$_2$ addition led to a 44% (18%) reduction than He at $X_0 = 0.45$ ($X_0 = 0.3$). The measurements were well reproduced by the numerical simulations. As shown in Fig. 5b, the quantitative difference in modelled peak $f_v$ between the H$_2$ and He-doped case reduced as $X_0$ decreased from 0.45 to 0.3, and became negligible as $X_0$ further decreased to be 0.24. Note again that the experimental data was not available for $X_0 = 0.24$, as the soot loading is too low to be accurately determined experimentally. However, we present the simulation results for the case with $X_0 = 0.24$ to clearly illustrate the $X_0$-dependence of H$_2$’s chemical effects (as compared to the case of $X_0 = 0.45$).

**Fig. 5.** (a) the measured soot scattering intensity and (b) predicted $f_v$ for H$_2$ and He-doped methane flames at different $X_0$ conditions.
This result suggests that the chemical effects from the addition of H\textsubscript{2} to CH\textsubscript{4} CDFs are sensitive to \(X_0\) conditions. Furthermore, the differences in C\textsubscript{2}H\textsubscript{4} and CH\textsubscript{4} CDFs even at the same \(X_0\) of 0.24 indicate that the chemical effect of the additional of H\textsubscript{2} on soot formation is dependent on the type of base fuel. To gain more insights into these observations, we performed detailed kinetic analysis to identify the mechanisms through which the addition of H\textsubscript{2} chemically inhibits the formation of soot in C\textsubscript{2}H\textsubscript{4} CDFs and to identify what causes the \(X_0\)-dependence of the chemical effect of H\textsubscript{2} in CH\textsubscript{4} flames. The following two sub-sections are respectively devoted to discussions of these two topics.

4.3 Chemical effects of H\textsubscript{2} addition in ethylene flames: Kinetic analysis

We now discuss the chemical effect of the addition of H\textsubscript{2} on soot formation in C\textsubscript{2}H\textsubscript{4} flames. In the present SF-type CDFs, the ultimate soot production depends on soot inception and surface reactions, both of which are coupled to the gas-phase chemistry of the flame via the formation of gas-phase soot precursors. In this regard, the effects of the addition of 20\% H\textsubscript{2} on important gas species are shown along with the effects in ethylene CDFs with addition of 20\% He in Fig. 6.
Fig. 6. Computed concentrations of important gas-phase species for neat and H₂- and He-doped ethylene CDFs ($X_0 = 0.24$).

Compared with the flame with the addition of He, the flame with the addition of H₂ has a higher C₂H₂ concentration (a). This is mainly due to the higher maximum flame temperature of the H₂-doped flame as compared with that of the He-doped flame (2221, 2247 and 2141 K for the neat C₂H₄, 20% H₂ and 20% He addition cases, respectively), which promotes the rate of ethylene pyrolysis and thus increases C₂H₂ formation. The H₂-doped flame also has a higher propargyl (C₃H₃) concentration (b). Rate of production (ROP) analyses showed that the formation channel for C₃H₃ is dominated by reaction 1 (R1), which was enhanced with addition of H₂ as compared with the addition of He. This can in turn be attributed to the fact that the addition of H₂ leads to higher concentrations of C₂H₂ in the C₃H₃ growth region, resulting in a higher rate of reaction of R1. Note the methylene (CH₂) is mainly formed through reaction 2 (R2) as follows:

\[
\begin{align*}
\text{C}_2\text{H}_2 + \text{CH}_2 & \rightleftharpoons \text{C}_3\text{H}_3 + \text{H} & \text{(R1)} \\
\text{C}_2\text{H}_2 + \text{O} & \rightleftharpoons \text{CH}_2 + \text{CO} & \text{(R2)}
\end{align*}
\]

The higher propargyl (C₃H₃) concentration in the H₂-doped flames partly contributes to its higher benzene (A₁) concentration (d) via the dominant A₁ production reaction, reaction 3 (R3). On the other
hand, the addition of H$_2$ also leads to higher A1 production than in the He-doped flame via reaction 4 (R4), the addition of C$_2$H$_2$ to C$_4$ species, due primarily to its enhanced C$_2$H$_2$ production. ROP analyses shows that reaction (R3) and (R4) accounts for 59% and 34% of total A1 production for the neat C$_2$H$_4$ flame, respectively (determined by taking the ratio of individual integrated value over the entire flame region to the total A1 production).

$2C_3H_3 \leftrightarrow A1$ \hspace{1cm} (R3)

$C_4H_5-2 + C_2H_2 \leftrightarrow A1 + H$ \hspace{1cm} (R4)

The H$_2$-doped flame also has a slightly higher pyrene (A4) concentration (e) than the He-doped flame has. However, ROP analysis shows that A4 production through the well-known HACA growth pathway actually decreased with addition of H$_2$. This is because in the HACA scheme [23, 24], the PAH radical (A$_r$-) formation reaction (R5) is the rate-limiting step while the increase in H$_2$ concentration due to addition of H$_2$ (c) favors the reverse reaction of (R5), which negatively contributes to the concentration of aryl radicals and in turn slows down the C$_2$H$_2$ addition reaction (R6). The increase in the H radical concentration with H$_2$ addition (c) is relatively small in the PAH growth region, which is believed to impose minor promoting effects on the PAH radical reaction (R5). Although not shown, evidence in support of this argument is found in the concentrations of A2 being lower in H$_2$-doped flames as compared with He-doped flames.

$A_i + H \leftrightarrow A_{i-} + H_2$ \hspace{1cm} (R5)

$A_{i-} + C_2H_2 \leftrightarrow A_iC_2H$ \hspace{1cm} (R6)

Nevertheless, A4 production through self-addition of the indenyl radical, C$_9$H$_7$, (R7) is obviously increased with the addition of H$_2$ as compared with the case of He addition and is shown to be the dominant contributor to the final increase in the A4 concentration.
Further ROP analysis shows that addition of H\textsubscript{2} improves the formation of C\textsubscript{9}H\textsubscript{7} through the reaction sequence of (R8)-(R10), which is initiated by enhancement of the C\textsubscript{2}H\textsubscript{2} species.

\begin{align*}
\text{2C}_9\text{H}_7 & \Leftrightarrow \text{A4} + \text{C}_2\text{H}_2 + \text{H}_2 & \text{(R7)} \\
\text{c-C}_5\text{H}_5 + \text{C}_2\text{H}_2 & \Leftrightarrow \text{C}_8\text{H}_5\text{CH}_2 & \text{(R8)} \\
\text{C}_8\text{H}_5\text{CH}_2 + \text{C}_2\text{H}_2 & \Leftrightarrow \text{C}_9\text{H}_8 + \text{H} & \text{(R9)} \\
\text{C}_9\text{H}_8 + \text{H} & \Leftrightarrow \text{C}_9\text{H}_7 + \text{H}_2 & \text{(R10)}
\end{align*}

Since PAH growth beyond A4 is assumed to be dominated by HACA routes, which are chemically inhibited with addition of H\textsubscript{2}, the consequence is the reduced A7 concentration in H\textsubscript{2}-doped flames (f). Note, despite the absence of experimental measurements in this work, the present PAH mechanism have been validated against the measured profiles of A1, A2 and A4 for similar ethylene CDF in a previous work [55]. Future quantitative measurements are necessary to validate the effects of H\textsubscript{2} addition on PAH species.

In the present PAH-based soot inception model, the lower concentrations of large PAHs (e.g., A7) in the H\textsubscript{2}-doped flames translates directly to lower soot inception rates, as compared with the case with addition of He. This is confirmed in Fig. 7a, where the indicated soot inception rate is the sum of the rates of all 36 dimerization reactions, among which the dimerization of PAHs larger than pyrene accounts for a significant proportion [56]. The maximum soot inception rate of H\textsubscript{2} doped flame is 15% lower than the He addition case. Consequently, the H\textsubscript{2}-doped flame has a lower soot-particle number density and thus less particle surface area is available for subsequent mass growth. Although not shown, the H\textsubscript{2}-doped flame has a smaller surface area density, \(A_s\) (cm\textsuperscript{2}/cm\textsuperscript{3}), than the He-doped flame has.

Figure 7b shows that addition of H\textsubscript{2} leads to a lower soot mass growth rate via the surface-HACA
mechanism, $\omega_{V,HACA}$ [$g/cm^3\cdot s$], which could be the reason for the lower soot production in H$_2$-doped flames. Note that the soot mass growth via physical PAH condensation was also included in our simulations although its contribution to the total soot mass was much smaller as compared to C$_2$H$_2$ addition reactions.

![Graphs](image)

**Fig. 7.** Computed soot inception rate (a), soot mass growth rate via surface HACA, $\omega_{V,HACA}$ (b), and the surface area normalized HACA growth rate, $\omega_{s,HACA}$ (c), of neat and doped ethylene CDFs ($X_0 = 0.24$).

In addition to the volumetric soot growth rate, $\omega_{V,HACA}$, which depends not only on the HACA reaction rate but also on the available surface area, we also present in **Fig. 7c** the surface area ($A_s$) normalized HACA growth rate, $\omega_{s,HACA}$ [$g/cm^2\cdot s$], which is calculated by dividing $\omega_{V,HACA}$ by $A_s$. Interestingly, the results show that although H$_2$-doped flames have higher C$_2$H$_2$ concentrations and temperatures (both of which are expected to improve the HACA reaction rate), they have comparable
peaks, $\omega_{s,HACA}$, with He-doped flames. This can be rationalized by noting that the higher H$_2$ concentration in the HACA growth region (Fig. 6c) tends to chemically inhibit the H-abstraction reaction (R11), which in turn reduces the rate of the mass addition reaction (R12). However, since addition of H$_2$ leads to a lower soot inception rate and therefore reduced available surface sites for the surface-HACA reaction to occur, the net result is a reduced $\omega_{V,HACA}$ and a lower SVF in H$_2$-doped flames. We thus conclude that the chemically inhibiting role of H$_2$ is dominant in the soot inception stage.

$$C_{\text{soot}H} + H \leftrightarrow C_{\text{soot}^*} + H_2$$  \hspace{1cm} (R11)

$$C_{\text{soot}^*} + C_2H_2 \Rightarrow C_{\text{soot}H} + H$$  \hspace{1cm} (R12)

### 4.4 H$_2$ addition in methane CDFs

We next investigate the $X_0$-dependence of H$_2$’s chemical effects on soot formation in CH$_4$ flames. It was shown in Fig. 5 that, for CH$_4$ CDF with $X_0 = 0.45$, H$_2$ has a stronger soot-inhibiting effect than He has. However, the effectiveness in inhibition of soot production was reduced at lower $X_0$ condition of $X_0 = 0.3$ and become negligible at $X_0 = 0.24$. To understand this interesting phenomenon, we analyze the soot inception and soot surface growth processes of H$_2$- and He-doped CH$_4$ CDFs.

Similar to the above analysis of C$_2$H$_4$ flames, we show the effects of the addition of H$_2$ or He on important gas-phase species relevant to soot inception in Fig. 8. We first consider CH$_4$ CDFs with $X_0 = 0.45$. Addition of H$_2$ leads to a higher maximum flame temperature than does addition of He (2648, 2690 and 2557 K for the neat CH$_4$, 20% H$_2$ and 20% He addition cases, respectively), which contributes to higher rates of fuel decomposition and C$_2$H$_2$ formation (a), as compared to the addition of He case. ROP analysis indicates that C$_3$H$_3$ production in the present CH$_4$ flames is dominated by
the reaction sequences of (R13)-(R14):

\[ \text{C}_2\text{H}_2 + \text{CH}_3 \rightleftharpoons \text{C}_3\text{H}_4\text{-P} + \text{H} \quad (\text{R13}) \]

\[ \text{C}_3\text{H}_4\text{-P} \rightleftharpoons \text{C}_3\text{H}_3 + \text{H} \quad (\text{R14}) \]

The lower \( \text{C}_3\text{H}_3 \) concentration in the \( \text{H}_2 \)-doped flame (b) is mainly due to its smaller \( \text{C}_3\text{H}_3 \) production rate through (R14). This is confirmed in Fig. 9 and can be attributed to the fact that \( \text{H}_2 \) addition leads to higher concentrations of H radicals (Fig. 8c) in the \( \text{C}_3\text{H}_3 \) production region, which chemically prevents the forward reactions of (R13)-(R14) and thus \( \text{C}_3\text{H}_3 \) production. Note the inhibiting effect of H radicals on \( \text{C}_3\text{H}_3 \) formation was also pointed out by Skeen et al. [96] in explaining the soot-free phenomena of the diluted ethylene/ oxygen CDF (with large stoichiometric mixture fraction of 0.78).

**Fig. 8.** Computed concentrations of important gas-phase species for neat and doped methane CDFs (\( \chi_0=0.45 \)).

It is also interesting to note that the main \( \text{C}_3\text{H}_3 \) formation pathway for the methane and ethylene flames we tested is different and is dominated by reaction (R14) and (R1), respectively. This is due primarily to the different fuel pyrolysis products of the two fuels: the abundance of the methyl (CH\(_3\)) radical in methane flame promotes via reaction (R13) the formation of propyne (C\(_3\)H\(_4\)-P), which is
then converted into C$_3$H$_3$ through reaction (R14). In contrast, the pyrolysis products in the ethylene flame are deficient of CH$_3$ radicals and, consequently, the main channel for C$_3$H$_3$ formation becomes the addition of methylene with acetylene (R1), which makes sense considering the relatively large amounts of C$_2$H$_2$ in ethylene flames.

![Production rate of C$_3$H$_3$ for H$_2$- and He-doped methane flames with $X_0$ of 0.45.](image)

**Fig. 9.** Production rate of C$_3$H$_3$ for H$_2$- and He-doped methane flames with $X_0$ of 0.45.

ROP analyses showed that benzene production of the present methane CDFs was dominated by C$_3$H$_3$ self-recombination (R4) (accounting for ~ 75% of total A1 production), the lower C$_3$H$_3$ production rate in the H$_2$-doped CH$_4$ flame results in its lower A1 mole fraction (Fig. 8d). Quantitatively, the peak mole fraction of A1 in the H$_2$-doped flame is 20% lower than that in the He-doped flame. In line with the HACA growth kinetics, H$_2$’s chemical inhibitive effect on A1 formation propagates to even lower mole fractions with larger PAHs (i.e., A4 (Fig. 8e) and A7 (Fig. 8f). Furthermore, A4 production via reaction (R7) (2C$_9$H$_7$ ⇌ A4 + C$_2$H$_2$ + H$_2$) is also chemically inhibited by the addition of H$_2$. This is because the production of C$_9$H$_7$ through the reaction sequences of (R15)-(R16) is chemically inhibited, which can be traced back to the reduction of C$_3$H$_3$ and the A1 concentration in H$_2$-doped flames. Note the maximum mole fraction of A7 in the H$_2$-doped methane flame is 44% lower than in the He-doped methane flame. It is also interesting to note the difference in
the main C₅H₈ formation channel between the methane (R15) and ethylene (R8-R9) flames.

\[
\text{A}_1 + \text{C}_3\text{H}_3 \Leftrightarrow \text{C}_9\text{H}_8 + \text{H} 
\]

\[
\text{C}_9\text{H}_8 + \text{H} \Leftrightarrow \text{C}_9\text{H}_7 + \text{H}_2
\]

(R15) (R16)

![Graph](image)

**Fig. 10.** Computed soot inception rate (a), soot mass growth rate through surface HACA, \(\omega_{v,HACA}\) (b), and the surface area normalized HACA growth rate, \(\omega_{s,HACA}\) (c), of neat and doped methane CDFs (\(X_O = 0.45\)).

The strong effects of H₂ in chemically inhibiting PAH growth naturally lead to a significant reduction in soot inception. As confirmed in **Fig. 10a**, the peak soot inception rate for the H₂-doped flame is nearly 75% lower than that for the He-doped flame. Consequently, notable decreases in the particle number density and in the available areas for surface growth are resulted. **Figure 10b** shows that the H₂-doped flame has an obviously lower HACA surface mass growth rate (\(\omega_{v,HACA}\)), which is responsible for its lower soot concentration. However, it is interesting to note that the surface-area
normalized HACA growth rates ($\omega_{s,HACA}$) are comparable between the H$_2$- and He-doped cases (Fig. 10c). This can be attributed to competition between the larger C$_2$H$_2$ concentration and the H$_2$ concentration in the H$_2$-doped flame, with the former (latter) tending to promote (inhibit) $\omega_{s,HACA}$ in the surface HACA mechanism. Therefore, we conclude that for methane CDFs with $X_O = 0.45$, the stronger soot reduction with the addition of H$_2$ is mainly due to H$_2$’s chemically inhibiting effects on the soot inception process, similar to the case for ethylene flames.

Figure 11 presents the gas-phase species relevant to soot inception for H$_2$- and He-doped methane CDFs with $X_O = 0.24$. The results show that although the H$_2$-doped flame again has higher concentrations of C$_2$H$_2$ (a) than the He-doped case, addition of H$_2$ chemically promotes the formation of C$_3$H$_3$ (b), leading to an opposite trend as compared to the case with $X_O = 0.45$. This interesting phenomenon is further elaborated in Fig. 12 where the total C$_3$H$_3$ production rates of H$_2$- and He-doped flames are compared at $X_O = 0.24$. This figure clearly shows that that the H$_2$-doped flame has a higher total C$_3$H$_3$ production rate than the He-doped flame has. This fact can be attributed to the higher concentration of C$_2$H$_2$ in H$_2$-doped flames, which increases C$_3$H$_3$ formation via reactions (R13)-(R14). Although addition of H$_2$ also leads to higher concentrations of H radicals (Fig. 11c), which tend to prevent C$_3$H$_3$ formation (similar to the case for $X_O = 0.45$), its effect is believed to be overwhelmed by the much higher concentration of C$_2$H$_2$ in H$_2$-doped flames at $X_O = 0.24$ (Fig. 11a). Note the peak C$_2$H$_2$ concentration in H$_2$-doped flames is around 40% higher than in He-doped flames at $X_O = 0.24$. In contrast, addition of H$_2$ leads to only 12% higher C$_2$H$_2$ as compared to addition of He at $X_O = 0.45$. By comparing the results between the cases of $X_O = 0.45$ and 0.24, we conclude that the change in $X_O$ mainly affects the concentrations of H and C$_2$H$_2$, which in turn, determine the relative C$_3$H$_3$ production between H$_2$- and He-doped flames through reactions (R13)-(R14).
The higher C$_3$H$_3$ concentration in the H$_2$-doped flames tends to promote benzene formation (Fig. 11d). This in turn mitigates the inhibitive effect of H$_2$ addition on the growth of large PAHs. As supported in Fig. 11e and f, the difference in the concentration of A4 and A7 is small between the H$_2$- and He-doped flame, as compared to the case with $X_O = 0.45$. This may help explain why the chemically soot-inhibiting effects of H$_2$ is largely mitigated for methane flames at lower $X_O = 0.24$.

![Fig. 11. Computed concentrations of important gas-phase species for neat and doped methane CDFs ($X_O = 0.24$).](image)

![Fig. 12. The C$_3$H$_3$ production rate for H$_2$- and He-doped methane flames with $X_O$ of 0.24.](image)
5. Concluding remarks

We experimentally and numerically investigated the effects of the addition of H$_2$ in the fuel stream of methane and ethylene counterflow diffusion flames and compared the results with the effects of the addition of He to isolate the chemical effects of H$_2$. Our results help us to explain the different inhibiting roles of H$_2$ and He in soot formation reported previously for ethylene and methane diffusion flames [11, 13, 16, 29]. Our major conclusions are as follows:

1. In ethylene flames, the addition of H$_2$ leads to stronger reduction of soot volume fractions than does the addition of He, demonstrating the chemically inhibiting role of H$_2$ in the sooting process. Kinetic analysis shows that the lower SVFs in H$_2$-doped ethylene flames (than in He-doped flames) is largely a result of H$_2$’s chemical inhibition of PAH growth and thus soot inception processes. The area-normalized surface growth rates of H$_2$- and He-doped flames are comparable, which can be attributed to the competing results of the larger C$_2$H$_2$ and H$_2$ concentrations in the H$_2$-doped flames, with the former (latter) tending to promote (inhibit) surface growth processes.

2. In methane flames, addition of H$_2$ is more effective than addition of He in reducing soot formation at $X_0 = 0.45$. However, the effectiveness of H$_2$’s soot inhibiting effect is largely mitigated at lower $X_0$ conditions (e.g., $X_0=0.3$ and 0.24). This result indicates the dependency of H$_2$’s chemical effects in soot formation in methane CDFs on $X_0$.

3. According to the kinetic model, for CH$_4$ flames with $X_0 = 0.45$, the addition of H$_2$ leads to higher concentrations of H radicals, which chemically inhibits the dominant C$_3$H$_3$ formation pathway through the reaction sequences of (R13): C$_2$H$_2$ + CH$_3$ $\leftrightarrow$ C$_3$H$_4$-P + H and (R14): C$_3$H$_4$-P $\leftrightarrow$ C$_3$H$_3$ + H. This in turn leads to the stronger reduction in benzene formation, PAH growth and the soot inception rate in the H$_2$-doped flames than in the He-doped flames. For the methane flames with
$X_O = 0.24$, the H$_2$-doped flame produces more C$_3$H$_3$ through (R13)-(R14) due to its much higher concentration of C$_2$H$_2$ in the C$_3$H$_3$ production region. This mitigates the inhibitive effect of H$_2$ addition on the growth of larger PAHs, leading to small difference in soot inception rate and finally the SVF between the H$_2$ and He-doped flame at $X_O = 0.24$ (as compared to the case of $X_O = 0.45$).

**Acknowledgements:**

This work was supported by the National Key R&D Program of China (2017YFC0211201), National Natural Science Foundation of China (51606136), Fundamental Research Funds for the Central Universities (WUT: 2017YB024), and the 111 Project (B17034). SHC was supported by King Abdullah University of Science and Technology.

**References**


[40] L. Figura, A. Gomez, Laminar counterflow steady diffusion flames under high pressure (P<=3MPa) conditions, Combust. Flame 159 (2012) 142-150.


