Mechanistic comparison of N\textsubscript{2} and H\textsubscript{2} dilution effects on soot formation processes in laminar ethylene diffusion flames

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**Abstract:** Fuel dilution is commonly used to reduce soot emissions from combustion engines or control carbon black morphology during fuel pyrolysis. Dilution has both physical and chemical effects on soot formation; however, the impact of fuel dilution on each soot formation process has not been fully understood yet. This study investigates the differing effects of dilution with H\textsubscript{2} and N\textsubscript{2} on particle inception and surface growth by hydrogen abstraction carbon addition (HACA) and polycyclic aromatic hydrocarbon (PAH) adsorption in ethylene/air laminar coflow diffusion flames. Applicable correlations are introduced to predict the conversion of carbon to soot at an accuracy of 96.5% at different dilution ratios. Both diluents result in significant reductions in HACA and PAH adsorption, up to 42% and 68%, respectively, at 40% dilution, with greater reductions for dilution with N\textsubscript{2}. For replacement cases, more reduction comes from a considerable change in the flame length, resulting in reduced high-temperature particle residence time. Combined, these effects significantly reduce HACA and PAH adsorption by up to 85% and 60%, respectively, for mixed replacement. Reduced acetylene and PAH concentrations for both gases, respectively, reduce HACA and PAH adsorption rates. Earlier in the flame, reduced PAH formation in the inception zone of the flame results in lower inception rates, producing fewer primary particles for subsequent growth processes. Comparing the two diluents, N\textsubscript{2} reduces acetylene and PAH concentrations by 12% and 18%, respectively, more than H\textsubscript{2}, and delays PAH formation in the flame, which delays inception and surface growth.

**Subjects:** Thermodynamics; Heat Transfer; Fluid Mechanics; Energy & Fuels; Nanoscience & Nanotechnology; Combustion

**Keywords:** soot; PAH; diffusion flame; dilution; hydrogen; nitrogen

1. Introduction

Reducing soot emissions and controlling carbon black yield during pyrolysis have been two main drivers of research on combustion-made carbonaceous nanoparticles. One way to achieve these goals is by adding diluent species to the fuel stream (addition) or replacing part of the fuel stream (replacement). Abhinavam Kailasanathan et al. (2013) measured soot precursor species in ethylene laminar coflow diffusion flames with four diluents (Ar, He, N\textsubscript{2}, and CO\textsubscript{2}) at elevated pressures. The CO\textsubscript{2} diluted flame had the lowest precursor concentrations that were three times less than that of the He diluted flame. They have also directly investigated the effect of these diluents on soot volume fraction (f\textsubscript{s}) and confirmed that CO\textsubscript{2} has the highest soot suppression effect, while He results in higher temperature and soot f\textsubscript{s}. This increase in temperature and soot was determined to
be caused by the higher thermal diffusivity of He (Kailasanathan et al., 2014). They concluded that lower soot yield is a result of increased oxidation rates rather than a reduction in precursor formation. Al-Qurashi et al. (2011) examined the effect of simulated Exhaust Gas Recirculation (EGR) via the addition of CO₂ species on an ethylene diffusion flame and engine intake. They reported a significant thermal effect of CO₂ on soot reactivity, a dilution effect that delays soot formation, and a chemical effect that suppresses the formation of large aromatic structures. The dilution effect of H₂ and CO₂ has also been investigated in flat premixed flames such as McKenna flames (De Iuilis et al., 2012; Naseri et al., 2017; Tang et al., 2016) with comparable findings to the coflow flames. Zhao et al. (2014) investigated ethylene laminar coflow diffusion flames with He and H₂ dilution and reported a reduction in soot number density and f_s by adding either He or H₂ diluents. This reduction was higher for replacement cases with up to 66% reduction in soot number density compared to the undiluted fuel flame. Ju et al. (2005) investigated the effects of N₂ dilution on soot formation in an inverse diffusion ethene flame and measured concentrations of polycyclic aromatic hydrocarbon (PAH), soot C/H ratio, and primary particle diameters to show reduced soot growth in the primary reaction zone. Sun et al. (2017) used laminar coflow diffusion flames of ethylene diluted with H₂ and N₂. Soot volume fraction and primary particle size measured by time-resolved LII (TiRe-LII) and flame temperature measured by two-line atomic fluorescence (TLAF) thermometry showed significant reduction for dilution with either diluent, with greater reduction for N₂ dilution and replacement. Soot formation in N₂ diluted ethylene diffusion flames has also been investigated at elevated pressures (Joo & Gülder, 2011; Liu et al., 2015). Comparable effects have been observed on the separated soot formation mechanisms with other nitrogenous diluents like ammonia (Shao et al., 2022). Overall, the measurements display the general trend that CO₂ dilution results in the greatest soot reductions, followed by N₂ and H₂ dilution, due to strong thermal and chemical effects.

Thus far, numerical simulations have focused on understanding the relative contributions of physical dilution, thermal, and chemical effects of diluents on soot formation by investigating N₂ and CO₂ dilution. Zhang et al. (2018) investigated the effects of N₂ and CO₂ on the oxidizer (O₂) flow of ethylene laminar coflow flames and reported soot reduction for both N₂ and CO₂, with a higher effect for CO₂ (for a maximum of 74% at f_s peaks) as a result of higher heat capacity. They concluded that the chemical effect of CO₂ enhances the oxidation of critical soot precursor species through increasing oxidizing species of O and OH. This chemical effect has been examined by Wang and Chung (2016) by introducing fictitious CO₂ as a chemically inert species in a counterflow ethylene flame. More numerical studies regarding the chemical effects of CO₂ have been conducted so far with similar findings (Gu et al., 2016; Liu et al., 2001). Numerical studies regarding N₂ dilution have indicated similar reducing effects of dilution on overall soot formation at atmospheric and high pressures (Liu et al., 2015; Smooke et al., 2005).

There have been numerical studies regarding the effects of H₂ dilution on soot formation focusing on the chemical versus thermal effects as well. Previous kinetic analyses have shown the chemical effects on different species production, including important precursor species such as C₃H₂ (Liu, 2014). In an early attempt to extract the chemical effect of H₂ dilution, Guo et al. (2006) investigated an ethylene coflow flame diluted with He or H₂. As He is a chemically inert gas, the chemical effect of H₂ has been assigned to the difference between He and H₂ results, showing that the chemical effect has the same order of effect on soot f_s as the dilution effect. Ying and Liu (2015) studied the H₂ effect as a fuel additive in a methane premixed flame. They reported that the chemical effect opposed the dilution and thermal effects that acted to reduce the formation of radicals. However, the chemical effect enhances the dilution and thermal effects of reducing C₃H₂ concentrations. Park et al. (2011) investigated the effects of H₂ addition on soot formation in laminar premixed C₃H₂ flames, with H₂ volume fraction varying from 10% to 50%. Although their model did not explicitly track the soot hydrogen content, they concluded that the abundance of H₂ molecules in the flame decreases soot surface active sites and consequently less particle growth. The effect of H₂ dilution on soot precursor species was investigated by F. Wang et al. (2015) in a study of hot ethylene coflow flames. The simultaneous effect of H₂ and other diluents has also
been numerically investigated by Gu et al. (2016) and Wang et al. (2018) in ethylene laminar coflow flames. Both studies have shown favorable dilution and chemical effects of H₂ on soot reduction, with a maximum of 35% reduction in peak soot fₛ at 50% H₂ dilution. The separation of chemical and dilution effects of H₂ has been investigated in a recent study by Qiu et al. (2020) by introducing a set of virtual species for a step-by-step decoupling of the chemical and thermal effects. Their results report a reducing influence from dilution and thermal effects, while the chemical effect of H₂ leads to higher soot formation through enhanced soot precursor formation. Similar work by Wang et al. (2021) showed that the chemical pathways leading to the formation of A1 aromatic rings are enhanced by the chemical effect of H₂ addition to methane and ethylene laminar diffusion flames. Similar behavior has been reported in premixed methane flames (Do et al., 2021). A summary of the above works of literature concerning the effects of N₂ and H₂ in diffusion flames is also provided in a more compact form in Table 1.

Overall, numerical investigations have focused on the effect of N₂ and H₂ dilution in isolation, rather than investigating the differences between these two diluents. Additionally, the focus has been on the differentiation of the physical dilution versus chemical effects of these diluents, rather than the effects on individual soot formation steps. Previous attempts have implemented different modeling approaches for the prediction of the dilution process (Khanehzar et al., 2022; Yen et al., 2019). However, in order to capture and compare the exact pathways of diluents’ effects on the soot formation mechanisms, soot models with refined and physics-based submodels are required. In this study, the differing effects of H₂ and N₂ dilution on the soot formation mechanisms of inception, HACA, and PAH adsorption surface growth in laminar ethylene/air coflow flames are

| Table 1. Works concerning effects of N₂ and H₂ in diffusion flames |
|-----------------|----------|-----------------|----------|-----------------|
| **Group**       | **Diluent** | **Flame**      | **Method** | **Main findings** |
| Zhao et al. (Zhao et al., 2014) | H₂, He    | Ethylene Laminar diffusion | experimental | Reduced soot fₛ for both diluents |
| Ju et al. (Ju et al., 2005)       | N₂        | Ethane laminar Inverse diffusion | experimental | Reduced soot growth in the primary reaction zone |
| Sun et al. (Sun et al., 2017)     | H₂, N₂    | Ethylene Laminar diffusion    | experimental | Reduced soot fₛ for both diluents; more reduction with N₂ |
| Zhang et al. (Zhang et al., 2018) | N₂, CO₂   | Ethylene Laminar diffusion    | simulation  | CO₂ reduces soot more than N₂ due to oxidizing precursors |
| Guo et al. (Guo et al., 2006)     | H₂, He    | Ethylene Laminar diffusion    | simulation  | H₂ reduces soot more than He due to having an extra chemical effect |
| Park et al. (Park et al., 2011)   | H₂        | Acetylene laminar premixed    | simulation  | Reduced particle growth from reduced active sites on particles |
| Wang et al. (Wang et al., 2018)   | H₂        | Ethylene Laminar diffusion    | simulation  | Favorable chemical effect of H₂ in soot reduction by reducing PAHs |
| Qiu et al. (Qiu et al., 2020)     | H₂        | Ethylene Laminar diffusion    | simulation  | Chemical effect increases soot by increasing soot precursors |
| Wang et al. (Wang et al., 2021)   | H₂        | Methane/Ethylene Laminar diffusion | simulation | Chemical pathways to A1 rings are enhanced |
investigated. For this purpose, a soot model is utilized that for the first time integrates the fundamentally improved submodels including the reversibility of inception and PAH adsorption, the physical phenomenon of surface shell formation, and refined tracking of hydrogen and PAHs that improves the prediction accuracy of PAH adsorption and HACA processes. Also, for a practical aim, the results are concisely interpreted in the form of two applicable correlations.

2. Flame and model description

2.1. Flame and geometry

The flames chosen for this investigation are the steady, non-smoking, co-flow diffusion flames studied by Sun et al. (2017). The flames are part of the international sooting flame (ISF) directory and are available as ISF-4 linked co-flow flames 2: Santoro-Adelaide burner. The burner has a fuel tube with an internal diameter of 10.5 mm surrounded by the oxidizer channel both discharging laminarily into atmospheric pressure with Reynolds numbers of less than 53. Different fuel stream flow rates are considered ranging from 0.207 to 0.518 liters per minute with a constant air supply rate. There are two sets of addition and replacement cases with varying volumes of H₂ and N₂ dilution. In cases with diluent addition, diluent gas is added to the fuel stream resulting in a higher flow rate. In replacement cases, the flow rate is held constant, while a volumetric percentage of the flow is replaced with the diluent. One of the main reasons to include two sets of addition and replacement dilution is to better separate the direct effect of the diluents from their effect on the flame geometry. While the replacement method simultaneously changes the flame geometry and the fuel composition, addition method maintains a constant geometry with changed fuel composition. It will later be discussed how the difference affects the important parameter of temperature–time history in the evolution of soot particles. A total of 14 flames with different ethylene/H₂/N₂ volumetric combinations are considered with 0%, 20%, 30%, and 40% of H₂ or N₂ dilution as well as mixed dilution with 20% N₂ and 40% H₂. It should be noted that the two undiluted flames in the addition and replacement sets have different ethylene flow rates. A summary of the flame conditions, ethylene/diluent concentrations, and flow rates are presented in Table 2.

2.2. Numerical model

The CoFlame code (Eaves et al., 2015, 2016), is utilized for discretization and solution of the governing equations and modeling of soot formation. The code solves the coupled transport equations of mass, momentum, energy, gas-phase chemical species, as well as soot aggregate number density, soot primary particle number density, and soot particle hydrogen number density. The chemical kinetic mechanism used for this investigation is the one originally presented in Eaves

| Table 2. Flame conditions and fuel concentrations |
|--------------------------------------------------|
| Flame | Ethylene (%) | H₂ or N₂ (%) | Total flow rate (l/m) | Flow velocity (cm/s) |
|-------|--------------|--------------|-----------------------|----------------------|
| Addition: | | | | |
| 0% | 100 | 0 | 0.207 | 4.0 |
| 20% | 80 | 20 | 0.259 | 5.0 |
| 40% | 60 | 40 | 0.345 | 6.6 |
| Mixed | 40 | 20% H₂ + 40% N₂ | 0.518 | 10.0 |
| Replacement: | | | | |
| 0% | 100 | 0 | 0.259 | 5.0 |
| 20% | 80 | 20 | 0.259 | 5.0 |
| 30% | 70 | 30 | 0.259 | 5.0 |
| 40% | 60 | 40 | 0.259 | 5.0 |
| Mixed | 40 | 20% H₂ + 40% N₂ | 0.259 | 5.0 |
et al. (2016). The solution method considers the discrete-ordinates method (DOM) to account for the radiation modeling (Eaves et al., 2016).

The computational domain for this investigation contains an axisymmetric field extending 13.7 cm in the axial and 4.7 cm in the radial direction. The computational domain does not include the fuel tube or conjugate heat transfer as results from these flames were not sensitive to this choice (Eaves et al., 2013). A top-hat velocity profile is used for the fuel and air inlets with zero gradient and free-slip boundary conditions at the outflow and outer radial boundary, respectively. Discretization of the governing equations is implemented using the finite volume method on a staggered grid. For this purpose, the computational domain is divided into 200 (z) × 86 (r) non-uniform control volumes. Due to the steady-state nature of the flame, pseudo-transient continuation is used to aid the convergence of the solution with convergence criteria of 0.001 residual for each variable.

The soot particle dynamics model is solved via a quasi-3D fixed sectional method with 35 logarithmically spaced sections. With the assumption of soot aggregates consisting of spherical identical soot primary particles, three transport equations of soot aggregate number density, primary particle number density, and soot hydrogen number density are solved within each section (Kholghy et al., 2016). The processes of inception, PAH adsorption, HACA surface growth, surface oxidation, coagulation, fragmentation, particle diffusion, and thermophoresis are included in the soot model. The soot model includes reversible inception (Eaves et al., 2017) with chemical bond formation (Kholghy et al., 2018), equilibrium-based PAH adsorption (Veshkini et al., 2016), hydrogen tracking to calculate surface hydrogen availability, surface shell formation (Kholghy et al., 2019, 2016), and HACA surface growth with an alpha of 0.5 for the portion of active soot particle surface sites available for chemical reactions (Eaves et al., 2016). It should be noted that only three PAHs (benzo-a-pyrene, benzo-a-pyrene radical, and benzo[ghi]fluoranthene) are assumed to participate in soot inception and PAH adsorption, and the impact of smaller PAHs is not considered (Eaves et al., 2015). A detailed description of the sectional method transport equations, solution methodology, and chemical mechanisms can be found in (Eaves et al., 2016).

3. Results and discussion
A total of 14 laminar co-flow flames of ethylene diluted with varying amounts of H₂ and N₂ for replacement and addition cases are simulated. This section starts with a comparison of the simulated results with measurements of flame temperature, soot volume fraction, and primary particle diameter (3.1). The comparison is followed by a discussion of diluents’ effects on soot formation mechanisms in terms of affected formation process rates, precursor species, and chemical pathways while differentiating the effects of N₂ and H₂ dilution (3.2).

3.1. Assessment of numerical model performance

3.1.1. Temperature
Figure 1 compares computed and measured (Sun et al., 2017) flame temperatures. Temperature data for the blue regions of the experimental side are not available and are not meant to represent low-temperature measurements. A comparison of the available regions shows acceptable agreement with the simulation results in terms of flame size and temperature distribution in the flame area. The reported temperature measurements are not corrected for soot radiation and have an uncertainty range of ±100 K. Therefore, the assessment of the numerical results is limited to qualitative trends for different diluents and dilution amounts, while the simulations have a quantitative difference of less than 80 K based on the maximum temperature, which is within the experimental uncertainty range. Similar comparisons for other dilution concentrations are available in the supplemental material (Figure A1).

3.1.2. Soot volume fraction
The simulations are further compared by the measurements of soot volume fraction (f_s) for undiluted and diluted flames shown in Figure 2, with further comparisons of 2D contours in the
Figure 1. Comparison of simulated temperature profiles (right half) with measurements (Sun et al., 2017; left half) of undiluted and diluted flames with addition cases (a) and replacement cases (b). The data only exists for limited portions of the flame area with an uncertainty of ±100 K without correction for radiation. However, for the available parts, simulated temperature qualitatively agrees with the experimentally observed changes with different dilution cases.

Figure 2. Computed (lines) and measured (symbols; Sun et al., 2017) soot volume fraction on flame wing (a,b) and centerline (c, d) at different heights above the burner for H2, N2, and mixed addition and replacement. Simulations capture the overall soot distribution through the flame height, peak point position and smaller variations downstream of the flames. Simulated flame positions are slightly higher than the measurements, approximately less than 5 mm (see supplemental material). The predicted peak values for flames wing and centerline are within 22% and 43% of the experimental data, respectively.

supplemental material (Figure A2). Figure 2 compares computed (lines) and measured (dots) soot $f_v$ along the flame wings and centerline. Here, the flame wing is considered as a line passing through the maximum soot $f_v$ at each axial height. For the wings (Figure 2 top), trends of the soot distribution are well predicted regarding the onset of the flame, peak points, and minor variations downstream of the peak. The predicted reduction of soot $f_v$ by dilution is also in good agreement for H2 and N2 in both addition and replacement cases. A slight flame height overprediction of less
than 5 mm is observed at the flame top points with the degree of overprediction decreasing for diluted flames. Simulation peak \( f_s \) is within 22% of the measurements. The axial location of peak \( f_s \) is similar but the magnitude of \( f_s \) decreases with diluent addition. This decrease is more evident for \( \text{N}_2 \) and mixed cases. While 40% \( \text{H}_2 \) addition reduces peak \( f_s \) by 22%, 40% \( \text{N}_2 \) and mixed additions reduce it by 34% and 48%, respectively. However, for replacement cases, flame height, and consequently the height of the peak \( f_s \) decrease significantly. For example, the flame height decreases from 11 cm to less than 4 cm when 20% \( \text{N}_2 \) and 40% \( \text{H}_2 \) replace the pure ethylene in the fuel inlet. This effect is also associated with a greater reduction in soot \( f_s \) for diluent replacement compared to the addition cases. For instance, a reduction of 5.7 ppm in peak soot \( f_s \) is predicted for the 20% \( \text{N}_2 \) and 40% \( \text{H}_2 \) replacement case. Similar to addition cases, replacement dilution with \( \text{N}_2 \) is again slightly more effective in soot reduction compared to \( \text{H}_2 \) dilution.

For the flame centerline (Figure 2 bottom), a good agreement with measurements is demonstrated as well for \( f_s \). The simulated results are within 43% of measurements based on the peak soot \( f_s \) values. Trends of soot distribution through the flame height and soot reduction with dilution are predicted well. A slight overprediction of height is seen at flame onset (HAB = 2 to 3.5 cm) and flame top (HAB = 4 to 10.5 cm) with differences from 0.3 to 1 cm. Similar to the wing results, \( \text{N}_2 \) dilution shows more reduction in soot \( f_s \) compared to \( \text{H}_2 \) dilution for both addition and replacement cases. Moreover, replacement results in lower soot \( f_s \) and causes flame height to reduce and centerline portion to shift downwards, closer to the burner. These effects are correctly captured by the simulation results.

3.1.3. Particle size

Figure 3 compares the reduction in the maximum soot primary particle diameter (\( d_p \)) at the centerline and the entire flame for addition and replacement cases on a log scale. At first glance, there is a gap between the measurement and simulation results by an order of magnitude. The experimental reference explicitly explains the large uncertainties of the LII method that leans towards larger \( d_p \) due to uncertainties arising from experiments (e.g., non-ideal spatial and temporal profile of laser beam) and assumptions in the LII models (e.g., non-aggregated and mono-dispersed particles), as well as inherent uncertainties of the LII models (Sun et al., 2017). These known uncertainties result in larger \( d_p \), which are more representative of a nonlinear combination of primary particle size and the number of primaries per aggregate (Boiarciuc et al., 2006). Despite high over-predictions associated with the LII measurement, the trends of dilution effect can be an effective factor in the assessment of the simulation results. For both
centerline and entire flames, the reducing trend of \( d_p \) due to the dilution is properly captured for both \( \text{H}_2 \) and \( \text{N}_2 \) cases. In fact, if both measurement and simulated results are normalized with their \( d_p \) of undiluted flame, simulations correctly capture the changes for both \( \text{H}_2 \) and \( \text{N}_2 \) with the results being within 8% of the measurements. Dilution with \( \text{N}_2 \) shows a greater effect on \( d_p \) reduction at a maximum of 7%. Also, replacement results in a higher reduction in \( d_p \) with a maximum of 10%. A normalized version of the data in this figure is also available in supplemental material (Figure A3).

### 3.2. Effect of \( \text{H}_2 \) and \( \text{N}_2 \) dilution on soot formation mechanisms

#### 3.2.1. Integrated process rates

To understand the effect of \( \text{H}_2 \) and \( \text{N}_2 \) dilution on the soot formation mechanism, the mass gains through the processes of inception, HACA surface growth, and PAH adsorption are separately followed on the path line of a particle starting its path from the burner to the top end of the flame. The gained mass is calculated through time integration of each formation rate (g/cm\(^2\)s) on its path, which will be termed accumulated mass. For easier comparison of the diluted cases, each process’s accumulated mass is normalized by the corresponding value from the undiluted flame.

Figure 4 shows normalized accumulated mass for the flame wings and centerline. For the wing, it is observed that \( \text{H}_2 \) dilution enhances mass accumulation by inception with a positive slope in addition cases, while \( \text{N}_2 \) reduces mass accumulation. The HACA and PAH adsorption mass contributions reduce for both dilution cases, with greater reductions for PAH adsorption with a maximum of 27%. The degree of the reductions increases for \( \text{N}_2 \) dilution and replacement cases. Mixed dilution cases have the greatest reduction in accumulated masses. For instance, the PAH adsorption ratio drops to less than 0.4 for 40% \( \text{N}_2 \) replacement and 0.15 for mixed...
replacement (40% H₂ and 20% N₂). With these results, it is understood that H₂ and N₂ have both resulted in lower soot by reducing the surface growth processes.

Accumulated mass ratios on the flame centerline also show a similar reducing trend. However, H₂ addition results in a slightly increased mass accumulation by HACA by less than 5%, while that of inception is reduced on the centerline. For N₂, on the other hand, all formation processes show a reduction, with a greater decrease for PAH adsorption. Dilution with N₂ reduces all of the processes’ mass ratios more compared to H₂. Similar to the flame wing, replacement leads to a steeper reduction than addition cases. For example, the accumulated mass ratio of HACA drops from 1.05 to 0.77 when comparing 40% H₂ additional and replacement cases. Reductions are higher for mixed replacement with the lowest PAH adsorption mass ratio equal to 0.22 of the undiluted flame.

3.2.2. Maximum HACA and PAH adsorption processes rates
Figure 5 shows changes in the maximum rates for HACA and PAH adsorption processes throughout undiluted and diluted flames for addition and replacement cases. Both processes show reduced rates for diluted flames, with N₂ having a greater reduction effect compared to H₂. At 40% dilution, while H₂ addition decreases the maximum HACA rate by 13%, N₂ results in a 27% reduction. Replacement results in a slightly steeper reduction of HACA rate for H₂ and N₂ compared to addition. The same trend with less difference applies to the maximum PAH adsorption rate.

3.2.3. Importance of temperature–time history
The previous figures display that fuel dilution reduces the two main mass-producing processes in soot formation. However, it is not clear why these reductions in HACA and PAH adsorption surface growth occur. It is well known that high-temperature particle residence time has a strong effect on soot formation. Figure 6 shows the parameter of temperature–time history versus dilution cases on the wings and centerline along with the peak soot f_v. Temperature–time history represents the total residence time of a soot particle at high temperatures in the flame and is defined by the following equation (Veshkini et al., 2015):

\[ T_v = \int_s T dt \]  

(1)

Where \( T \) is temperature and \( s \) is the path (typically through the centerline or wing). Due to its integration over the path, this parameter is dependent on the flame height. Comparing the replacement and addition cases, a greater reduction is observed for replacement cases, while this reduction is relatively low for the addition cases. This is also similar to the flame height.
reduction mentioned earlier and in the supplemental material. Flame height reduction is in line with Roper’s analysis of the fuel flow rate and the flame height (Roper, 1977). Roper’s correlation states that a lower fuel inlet rate to the burner results in a shorter flame due to the competition between axial momentum and radial diffusion (Roper, 1977). For replacement cases, where diluent reduces the ethylene inlet rate, such flame height reduction and consequently greater reduction in temperature–time history occur. Matching trends of temperature–time history and peak soot volume fraction indicate the source of reduction in the formation processes (HACA and PAH adsorption). Due to a shorter flame, soot particles spend less time in hot reactive areas which leads to less surface growth through HACA and adsorption of PAHs on particle surfaces. The correlation between temperature–time history and soot formation reduction is more evident in replacement cases where significantly changed flame geometry demonstrates its dominance in soot formation suppression. This effect with roots in the changes in the temperature–time history is singled out by comparing the flame geometry between the replacement and addition cases. However, for addition cases and specifically N₂, soot volume fraction has a more rapid reduction compared to temperature–time history, indicating that more effects are acting to reduce soot formation beyond changes in the flame geometry.

3.2.4. Carbon to soot conversion

A practical interpretation of soot results that removes the effect of varying fuel flow rates can be defined as the conversion of carbon to soot. At each HAB, the soot mass flow rate \( \dot{m}_{\text{soot}}(z) \) can be calculated from a radial integration as below:

\[
\dot{m}_{\text{soot}}(z) = \int (u_{\text{soot}})(\rho_{\text{soot}})(f_v)(2\pi r)dr
\]
Figure 7. Maximum carbon to soot conversion for addition and replacement flames at different diluent concentrations. Higher amount of diluent results in linear reduction of conversion with higher slope for N$_2$ compared to H$_2$ cases.

Where $u_{\text{soot}}$ is the axial velocity of the soot particles, $\rho_{\text{soot}}$ is the soot particle density, and $f_s$ is the soot volume fraction. By dividing the soot mass flow rate by the mass flow rate of carbon from the fuel inlet, carbon to soot conversion is calculated at each HAB.

The maximum carbon-to-soot conversion for dilution cases is presented in Figure 7. Values from simulations are within 17% of the values calculated from the experimental data, and the trends are relatively captured. The maximum conversion typically occurs at the same HAB as the maximum $f_s$. An increase in diluent percentage reduces the conversion. In agreement with the results in earlier sections, N$_2$ has a higher reducing effect on carbon to soot conversion. For addition cases, undiluted flame results in 12.51% conversion, while it decreases to 11.03% and 9.25% for 40% H$_2$ and N$_2$ additions, respectively. The slope of conversion reduction is higher for replacement cases, from 14.31% conversion for undiluted flame down to 8.94% and 7.76% for H$_2$ and N$_2$ at 40% replacement. The conversion reduction follows a linear trend for each of H$_2$ and N$_2$ at addition and replacement cases. Mixed dilutions mark the highest conversion reductions, down to 4.1% at maximum. However, the conversion of the mixed dilution does not lie on the linear trend of single diluent cases, which refers to the synergetic effect from the presence of both diluents in the flame.

The information from Figure 7 can be integrated into the following linear correlations for addition and replacement cases based on the concentration of the diluent in the fuel stream (excluding the mixed diluents).

Addition: \[ \text{Conversion}(\%) = 12.66 - 0.0369[H_2](\%) - 0.0814[N_2](\%) \] (3)

Replacement: \[ \text{Conversion}(\%) = 14.47 - 0.1327[H_2](\%) - 0.1631[N_2](\%) \] (4)

The correlation lines fit within 3.5% of the numerical results.

3.2.5. Differentiating the effects of H$_2$ and N$_2$ dilution

To differentiate the effects of H$_2$ and N$_2$ dilution on soot, key species such as acetylene and PAH are investigated. Figure 8 shows the distribution of maximum concentration of benzo[a]pyrene as the main PAH contributing to PAH adsorption vs. height above burner (HAB) for undiluted and diluted flames at 40%. Two peaks are observed corresponding to lower and higher regions inside the flame approximately at HAB = 1 cm and 2 cm, respectively. The first peak located at the lower flame region corresponds to the flame wing, where the first primary particles are incepted as a result of PAH collision. The second peak is located on the flame centerline at the higher end of the inception zone. Any PAH reduction in the region between these peaks reduces the inception of the new particles on the flame wings and centerline that will later go through the growth
processes. Dilution shows a greater reduction at the first peak (flame wings). This dilution effect was observed earlier in Figure 4 showing greater reductions in the processes for the flame wings compared to the flame centerline. A comparison of the effects of H₂ and N₂ on this region shows a considerable reduction in PAH concentration as well as a delay for the first peak. In the case of N₂ addition, this delay and reduction are even more pronounced compared to H₂ addition. H₂ and N₂ addition, respectively, result in a 25% and 65% reduction in PAH concentration at the location of the first peak for undiluted ethylene. Given that the flame height remains unchanged (Figure 1-addition), this higher delay in PAH formation by N₂ dilution results in a shorter available path in the flame for inception and consequently surface growth processes. Overall, the soot formation region of the flame is shorter due to the dilution. Additionally, lower PAH concentration

Figure 8. Maximum PAH concentration along flame height for undiluted flame and diluted flames at 40% addition (a) and replacement (b). First peak lies on flame wing at lower HAB and zones of soot inception onset. H₂ and N₂ addition, respectively, result in 25% and 65% reduction in PAH concentration at the location of first peak for undiluted ethylene. The first peak is delayed by H₂ and greater by N₂ addition, leading to shorter inception and consequently growth zone through flame height. H₂ and N₂ replacement, respectively, result in 19% and 30% reduction in PAH concentration at the location of first peak for undiluted ethylene. The first peak and top end of the graph are significantly closer for both H₂ and N₂ replacement, leading to shorter inception and consequently growth zone through flame height.

Figure 9. Primary particle number density at HAB = 1 cm on flame wing for undiluted flame and diluted flames at 40% addition and replacement. H₂ addition significantly declines the number density to 52% of its value for undiluted ethylene, followed by N₂ addition reducing it to 43%. At replacement, H₂ reduces the number density to 69% of its value for undiluted ethylene, followed by N₂ dilution reducing it to 61%.
after the inception zone leads to less surface growth from PAH adsorption. In this regard, N₂ shows a greater reduction, having a considerably lower PAH concentration between the two peaks. For replacement cases, the same reduction is observed as well as a shortened span which is due to the changed geometry of the flames (Figure 1-replacement).

The effect of reduced PAH concentration at the inception region is shown in Figure 9 in form of the primary particle number density at the location of the first peak in the previous figure (HAB = 1 cm). The number of primary particles dramatically drops for both H₂ and N₂ at addition and replacement cases. The first stage of reduced soot formation is observed at this point, where fewer PAH are adsorbed.

Figure 10. Maximum acetylene concentration along flame height for undiluted flame and diluted flames at 40% addition (a) and replacement (b). Despite a longer acetylene presence for diluted flames in addition cases, acetylene concentration is constantly lower than its value at undiluted ethylene flame at flame parts corresponding to growth zones. The difference peaks at 8% for H₂ and 20% for N₂ addition. With replacement, acetylene concentration of diluted flames is lower than its value at undiluted ethylene flame. Inside the flame height, the concentration difference peaks at 15% for H₂ and 21% for N₂ replacement. Also, the top end of acetylene presence is significantly lowered by both H₂ and N₂ at approximately 40%.

Figure 11. Main chemical pathways from ethylene to C₂H₂ and benzo[a]pyrene for an equivalent perfectly stirred reaction modeling with the temperature and residence times at the onset of soot formation in the current flames. Arrows in red indicate reactions where hydrogen plays an enhancing role with the species production rate (mole/cc.sec) of 40% dilutions with H₂ and N₂. Arrows with dashed lines indicate collapsed series.
Acetylene is another key species in the formation of soot and specifically in the HACA surface growth process. The distribution of maximum acetylene concentration vs the flame height for undiluted ethylene and diluted flames at 40% is shown in Figure 10. Reduction due to both addition and replacement by H₂ and N₂ is observed. The addition of H₂ causes a maximum of 8% reduction in acetylene concentration, while N₂ results in a 20% reduction. Reduced acetylene at the mid-height of the flame coincides with the regions of surface growth and mainly affects the HACA process. Together with the reduced number of incepted particles, acetylene reduction is considered a principal reason for the decreased HACA mass accumulation observed previously in Figure 4. Similar to previous effects, N₂ dilution shows a greater effect compared to H₂, having more than twice the reduction as H₂ in addition cases. For replacement cases, acetylene reduction is accompanied by reduced flame height which minimizes the potential of surface growth due to the HACA process.

Further investigation of the difference between H₂ and N₂ dilution effect on soot formation requires understanding why N₂ dilution results in reduced benzo[a]pyrene (BAPPYR) and C₂H₂ concentrations. In this regard, a set of chemical analyses is carried out in the form of equivalent perfectly stirred reactor (PSR) modeling. Different cases, each corresponding to a HAB at lower flame regions, display the differing effect of H₂ and N₂ dilution on flame chemical pathways. A collapsed version of pathways from fuel to the main components of soot formation, including acetylene and benzo[a]pyrene as the main PAH, is depicted in Figure 11. Chemical paths that hydrogen dilution enhances compared to N₂ dilution are marked with red arrows. The species production rates (mole/cc/sec) of 40% dilutions with H₂ and N₂ are also given on these arrows at the conditions of the onset of soot formation. This includes all the pathways from pure ethylene to acetylene. Therefore, the presence of hydrogen chemically enhances the formation of acetylene and consequently PAH. However, hydrogen abundance in H₂ cases has a physical diluting effect, which lessens this chemical effect to a value lower than the undiluted case. In the case of N₂ dilution, the reduced hydrogen and physical diluting effect are present at the same time, where the lowest species formation rates are recorded.

A more detailed table containing the formation rates of species from Figure 11 in undiluted and diluted flames is available in the supplemental material. As a representation, Table 3 shows the formation rates of acetylene and benzo[a]pyrene PAH from three dilution cases (undiluted, 40% H₂, and 40% N₂ addition) at conditions corresponding to three different HABs from lower flame conditions.
heights. While the H₂ diluted case closely follows the undiluted ethylene, N₂ dilution requires a higher height and temperature to reach the same level of formation rates as undiluted and H₂ cases. In other words, N₂ delays the reactions in the pathway to a higher height inside the flame. This delay in PAH formation and its effects on soot formation have already been observed and discussed in Figure 8. Therefore, another different behavior of H₂ and N₂ dilution is that N₂ comprises a low level of hydrogen in chemical reactions with its diluting effect and delays the formation of key species that reduce the consequent mechanisms of soot formation.

3.3. Conclusion
Dilution effects of H₂ and N₂ on soot formation mechanisms are numerically investigated in ethylene/air laminar coflow diffusion flames. A set of 14 combinations of diluent addition and fuel replacement cases are considered to compare the separate and combined effects of H₂ and N₂ on inception, HACA, and PAH adsorption surface growth. The CoFlame code is utilized with the results well validated against experimental data. The main conclusions of this study are:

- For both H₂ and N₂, mass contributions from HACA and PAH adsorption reduce for all dilution cases. These reductions increase for replacement cases compared to addition cases. Also, dilution with N₂ results in a greater reduction in HACA and PAH adsorption mass contributions compared to H₂ dilution.
- A comparison of the addition and replacement cases shows that the primary source of the diluent’s effects on soot reduction comes from the changes in the flow geometry that affect the parameter of temperature–time history.
- H₂ and N₂ dilution by replacement changes the flame geometry and results in reduced temperature–time history. Thus, soot particles have less residence time at high temperatures, leading to less soot growth. This reduction is the primary cause of the reduced soot mechanism contributions.
- The addition of H₂ and N₂ results in decreased PAH concentration at lower flame HAB, where the inception process is dominant. This reduction results in a lower number of primary particles that later undergo the growth processes. N₂ addition has a greater reduction in this regard compared to H₂ addition.
- N₂ addition causes another decrease in acetylene concentration at the regions of HACA growth. Together with lower PAH concentration, N₂ dilution results in lower growth rates and consequently lower soot fₕ compared to H₂ dilution.
- The origin of different effects from H₂ and N₂ dilution is found in the chemical reactions, where less hydrogen in N₂ dilution delays the formation of key species like PAH and acetylene to higher heights in the flame, leading to less residence time for soot inception and growth.
- A pair of correlations is introduced to relate the carbon to soot conversion to the diluent concentration in the flame for addition and replacement cases.

As an extension to the present work, further research should focus on different combinations of fuel types and diluents. Additionally, investigations should target the effect of varying pressure on hydrogen fuel stream dilution.

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