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Effects of hydrogen and helium addition to fuel on soot formation in an axisymmetric coflow laminar methane-air diffusion flame

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1. Introduction

Emission of pollutants formation from combustion systems has become a great public concern in recent years. Emission of particulates (soot) from conventional hydrocarbon fuelled combustion devices into the environment has been identified to be detrimental to human health and suspected to be an important contributor to climate change. These concerns have drawn renewed interests in finding alternative fuels. In this context, hydrogen is considered the most promising clean energy source for the long run, even though several difficulties, which currently prevent its widespread use for power generation and transportation, are yet to be overcome. As an intermediate solution, some attention is devoted to particular blended fuels, like hydrogen/hydrocarbon mixtures. The use of these fuels has been found to result in improved combustion performance, both in terms of combustion ignitability and stability and in terms of pollutants emission reduction (NO\textsubscript{x} and soot). The features of these fuels are difficult to predict due to the complex and nonlinear nature of chemical kinetics and multi-component diffusion processes. Much work is still required to understand the physical-chemical mechanisms of the combustion of hydrogen/hydrocarbon mixed fuels.

To date there have been only few studies in the literature on the influence of hydrogen addition to fuel on soot formation in laminar hydrocarbon diffusion flames. Tesner found that dilution of natural gas by hydrogen slows down the formation of carbon black particles during thermal decomposition [1]. In an investigation of soot formation in laminar cylindrical methane diffusion flame, Tesner et al. [2] showed that addition of hydrogen or nitrogen to fuel reduces soot yield with nitrogen is more effective than hydrogen. Dearden and Long [3] experimentally investigated the influence of hydrogen and nitrogen addition to fuel on the sooting rate of laminar ethylene and propane diffusion flames established on a Wolfhard-Parker burner. They found that addition of hydrogen to fuel reduces the sooting rate in both flames and in the case of ethylene hydrogen is more effective than nitrogen. Through measurements of the influence of various additives to fuel on the soot-particle inception strain rate in counterflow C\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{8}, and C\textsubscript{4}H\textsubscript{10} diffusion flames, Du et al. [4] found that addition of H\textsubscript{2} to these hydrocarbon fuels substantially reduces the soot inception strain rate. Their results also indicated that addition of helium to fuel is somewhat more effective than H\textsubscript{2} in suppressing soot formation, despite addition of H\textsubscript{2} results in a higher flame temperature. The chemically inhibiting effect of H\textsubscript{2} addition to fuel on soot formation was further investigated experimentally by Gülder et al. [5] in laminar coflow C\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{8}, and C\textsubscript{4}H\textsubscript{10} diffusion flames with and without dilution by H\textsubscript{2} and helium. Their experimental results showed that hydrogen is much more effective than helium in suppressing soot formation when added to C\textsubscript{2}H\textsubscript{4}, but it does not show additional effectiveness when added to C\textsubscript{3}H\textsubscript{8} or C\textsubscript{4}H\textsubscript{10}. They suggested that the additional effectiveness of hydrogen addition to C\textsubscript{2}H\textsubscript{4} compared to that of helium addition is due to the chemical effect of hydrogen. Very recently, Guo et al. [6] numerically investigated the effect of hydrogen and helium addition to the C\textsubscript{2}H\textsubscript{4} flame experimentally investigated by Gülder et al. [5] using a very detailed reaction mechanism and a two-equation soot model. Their numerical results reproduce the chemical effect of hydrogen addition on reducing the soot yield observed experimentally by Gülder et al. The primary chemical effect of hydrogen addition to C\textsubscript{2}H\textsubscript{4} was identified to be the decrease in the hydrogen atom concentration in the soot surface growth regions, which leads to a reduced surface active site number density according to the hydrogen...
abstraction acetylene addition (HACA) mechanism for soot surface growth [7]. While the chemical effect of hydrogen addition to fuel on soot formation reduction in C₂H₄ flame has been investigated experimentally by Gülder et al. [5] and numerically by Guo et al. [6], such effect has not been investigated in CH₄ flame.

In this work the influence of hydrogen addition to fuel on soot formation in a laminar coflow methane/air diffusion flame is investigated both experimentally and numerically. In particular, soot volume fraction and soot temperature field measurements were performed in a coflow laminar methane diffusion flame with and without hydrogen and helium addition. Numerically, the governing equations in axisymmetric cylindrical coordinates were solved using the finite volume method. To unambiguously show the different influence of hydrogen addition to methane and ethylene on soot formation relative to that of helium, the identical gaseous reaction mechanism and soot model to those employed previously by Guo et al. [6] were used. A comparison between the present experimental and numerical soot volume fraction also provides direct evidence on how the soot model used by Guo et al. [6] to the C₂H₄ diffusion flame performs when applied to the methane flame investigated here, i.e., the generality of the soot model.

2. Experimental Method and Numerical Model

Experiment:
The principle of soot measurement was based on a two-color flame emission technique. The measured intensity of soot emission \( I_s \) at a wavelength \( \lambda \) is expressed as

\[
I_s = \varepsilon_{s\lambda}(f_s)I_{b\lambda}(T)\tau_{b\lambda}
\]

where \( \varepsilon_{s\lambda} \) is the soot emissivity, \( \tau_{b\lambda} \) is the transmission of the optical system, \( I_{b\lambda} \) is the spectral blackbody radiation intensity at the soot temperature \( T_s \). Symbols c, \( h \), and \( k \) are respectively the speed of light, the Planck constant, and the Boltzmann constant. For a uniform layer of soot of length \( L \) at a volume fraction \( f_s \), the emissivity is given as

\[
\varepsilon_{s\lambda} = 1 - \exp(-K_{abs}\lambda)
\]

where the soot absorption coefficient \( K_{abs} \) is related to soot volume fraction and wavelength through

\[
K_{abs} = \frac{6\pi E(m)\lambda f_s}{\lambda I_{abs}}
\]

where \( E(m) \) is the soot absorption function and \( I_{abs} \) is the natural length of absorption. To obtain the absolute measurements, the light emitted from soot needs to be compared with that emitted from a calibrated lamp at a known temperature \( T_{lamp} \),

\[
I_l = \varepsilon_{l\lambda}(T_{lamp})I_{b\lambda}(T_{lamp})\tau_{l\lambda}
\]

Using the same optical arrangement, the transmission of the optical system remains the same, regardless the source of radiation, i.e., \( \tau_{b\lambda} = \tau_{l\lambda} \). By measuring the emission intensities at two wavelengths, \( \lambda_1 \) and \( \lambda_2 \), from both sources (soot and the calibrated lamp), one can relate the soot temperature to other known variables as

\[
T_s = -C_2\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)\ln\left[I_{l\lambda_1}I_{abs\lambda_1}\varepsilon_{l\lambda_1}\right] + C_2\frac{1}{\tau_{lamp}}T_s\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)^{-1}
\]

by eliminating the system transmissions at the two wavelengths through the ratio of these emission intensities. Once the soot temperature is available, the soot volume fraction can then be obtained as, by the ratio of the two emission intensities at either \( \lambda_1 \) or \( \lambda_2 \) (the results is identical),

\[
f_s = \frac{1}{L} I_s \frac{I_{abs}}{I_l} \varepsilon_{l\lambda}(T_{lamp}) \exp\left[\frac{hc}{k\lambda}\left(\frac{1}{T_s} - \frac{1}{T_{lamp}}\right)\right]
\]

The collected images were processed by a MATHCAD program. Ten different individual images, taken at both wavelengths, were binned (2×2), symmetrized and averaged. The average images were processed, row-by-row, by an Abel inversion procedure in order to obtain local values of both emission signals [10]. Then the two inverted images were ratioed and compared with the corresponding ratio of the intensities measured from the calibration lamp. Finally, the 2D distribution of soot temperature (\( T_s \)) and of soot
volume fraction \((f_v)\) were obtained according to Eqs.(5) and (6) with a spatial resolution of 98 pixels/cm.

Fig. 1 Schematic of the optical set-up.

The atmospheric pressure laminar coflow CH\(_4\)/air diffusion flame investigated in this study was established using a co-annular burner very similar to those used by Santoro et al. [8] and Gülder et al. [5]. The fuel (CH\(_4\)) is delivered through the inner fuel tube with an inner diameter of 10 mm. Air is delivered through the annular region between the fuel tube and the air tube of 100 mm in diameter. The burner was constructed with a honeycomb placed inside the outer tube to minimize flow disturbance that may cause flame instability. The flow rates for methane and air were maintained constant under all conditions at 0.38 l/min and 35.4 l/min, respectively. Both fuel and air were delivered at room temperature. The corresponding mean velocity of the fuel stream is about 8.06 cm/s for pure CH\(_4\). The air flow rate was sufficiently high to have negligible influence on the visible flame height. Under these conditions, the flames are quite stable and reproducible with the luminous flame height about 65 mm. This visible flame height is nearly identical to that of the ethylene flame investigated previously [5,6].

**Numerical Model:**

The numerical model used in this study is identical to that used previously by Guo et al. [6]. Therefore, the different influence of hydrogen addition to methane and ethylene on soot formation, if any, relative to that of helium can be unambiguously revealed. The combustion reaction mechanism is essentially that developed by Appel et al. [7], which consists of 101 species and 544 reactions. The only minor modification made here is that Ar was replaced by He. Soot was modelled using the simplified semi-empirical two-equation model described in detail by Guo et al. [6]. Briefly, two additional transport equations for soot mass fraction and soot particle number density per unit mass are solved. The nucleation process was assumed to be the result of PAH coagulation, i.e., the collision (coalescence) of two pyrene molecules forms a dimer. The surface growth and oxidation were assumed to follow the H-abstraction acetylene addition (HACA) mechanism [7]. It is worth pointing out that the parameter \(\alpha\), which represents the fraction of active surface sites available for surface growth, was adjusted by Guo et al. [6] as \(\alpha = 0.0045 \exp\left(\frac{9000}{T}\right)\) to match the predicted peak soot volume fraction in agreement with experiment in the C\(_2\)H\(_4\) flame (about 8 ppm). This value was unchanged in this study for the purposes mentioned earlier. The three most important species for soot oxidation, i.e., O\(_2\), O, and OH, were all included in the model. Further details of the numerical model can be found in [6].

The dimensions of the computational domains are 3.23 cm in the radial direction (r) and 9.8 cm in the streamwise direction (z). The computational domain is resolved by using 161×80 non-uniform grids in the radial and streamwise directions, respectively, with finer grids placed in the near burner exit region to resolve the sharp gradients while minimizing the computational cost.

**3. Results and Discussion**

The calculated distributions of temperature with and without 30% H\(_2\) or 30% He dilution are compared (not shown). It was found that 30% addition of H\(_2\) or He to CH\(_4\) only slightly increases or decreases the peak temperature by about 7 K and 27 K, respectively. Overall the effect of moderate amount of H\(_2\) or He addition to CH\(_4\) (up to 40% considered here) has insignificant influence on the flame temperature.

The predicted and measured distributions of soot volume fraction with and without 30% addition of H\(_2\) and He are displayed in Figs.2 and 3, respectively. Several obvious observations can be made when the predicted soot volume fraction distributions are compared to the measured ones. First, soot is predicted to appear at a much higher location than the measurement. However, both the prediction and measurement indicate that soot appears at a higher location when H\(_2\) or He is added to the fuel, especially in the case of He addition. Secondly, the model predicts that the peak soot volume fraction always occurs in the annular region of the soot shell, Fig.2. However, the experimental data indicates that the peak value always occurs on the flame centerline under the present conditions. In this regard, the present experimental results are in
agreement with other experimental results reported previously in the literature [9-11] in CH$_4$ coflow diffusion flames of comparable size. Thirdly, the measured distributions show that there is significant amount of soot in the centerline region between $z = 4.6$ and $6.4$ cm, while the model predicts that soot only occupies a narrow region along the flame centerline roughly between $z = 5.5$ and $6.2$ cm. Fourthly, the measured peak soot volume fraction in the pure CH$_4$ flame is about $0.58$ ppm, which is reasonable agreement with, though somewhat higher than, those reported in [9-11]. The calculated peak soot volume fraction in this case, however, is only about $0.05$ ppm, i.e., an order of magnitude lower than the experimental data. Such a large difference between the calculated and the measured peak soot volume fractions are not expected given the fact that the soot model, along with the detailed gaseous reaction mechanism, predicts almost identical peak soot volume fraction to the experimental data in the C$_2$H$_4$ flame investigated by Guo et al. [6]. Clearly, the soot model employed here and in [6] is not robust when applied to different hydrocarbon fuels, in terms of the absolute values of soot volume fraction.

![Fig.2 Comparison of the calculated soot volume fraction distributions with and without 30% dilution.](image)

![Fig.3 Comparison of the measured soot volume fraction distributions with and without 30% dilution.](image)

It is evident from the results shown in Figs.2 and 3 that addition of either H$_2$ or He reduces the soot volume fraction with He is apparently more effective than H$_2$. This observation is very different from the previous experimental finding that H$_2$ is significantly more effective than He to suppress soot when added to C$_2$H$_4$. The results shown in Figs.2 and 3 also indicate that the visible flame height is slightly increased by H$_2$ addition, but otherwise remains almost unchanged by He addition.

![Fig.4 Comparison of measured and calculated flame cross section area integrated soot volume fractions at different levels of H$_2$ addition.](image)

To provide a direct comparison on the influence of dilution by H$_2$ and He on soot formation, the flame cross sectional area integrated soot volume fraction along the flame height defined as

$$ F_v(z) = 2\pi \int_{r} f_v(r,z) \, dr $$

under different levels of dilution are evaluated. The influence of H$_2$ dilution on this quantity is shown in Fig.4. Although quantitatively the predicted cross sectional area integrated soot volume fractions are much lower than the experimental values by about a factor of 15, the model qualitatively reproduces the main
features of the experiment shown in Fig.4(a). The influence of He addition to fuel on $F_v(z)$ is qualitatively similar to that of H$_2$ (not shown).

To further quantify the effect of dilution by H$_2$ and He on the soot yield, the total amount of soot volume fraction defined as

$$S_v = \int_0^\infty F_v(z) dz$$

is evaluated and compared under different levels of dilution. Because the predicted soot volume fractions are about an order of magnitude lower than the experimental data shown earlier, only the normalized total soot volume fractions (by that of the pure CH$_4$ flame) are compared in Fig.5 to illustrate the relative effectiveness of H$_2$ and He on soot suppression in the coflow CH$_4$ diffusion flame. Although there exist somewhat significant quantitative differences between the predicted and the measured normalized total soot volume fractions, the soot model used here correctly reproduced the overall relative effectiveness of H$_2$ and He revealed experimentally, i.e., H$_2$ is significantly less effective than He to soot suppression in CH$_4$ diffusion flame. It is also worth pointing out that the model predicts a much stronger reduction in the total soot volume fraction than the experiment when a small amount of H$_2$ (up to 10%) is added to CH$_4$. Between 10 to 20% H$_2$ addition to CH$_4$, the model predicts that the total amount of soot in the flame remains more or less the same. As more H$_2$ is added beyond 30%, the predicted total amount of soot starts to decrease again, but at a rate slower than the experiment. On the other hand, however, the experimental data show a monotonically decreasing total amount of soot, though somewhat non-linear, as more H$_2$ is added, i.e., the total soot volume fraction decreases at a faster rate when the added amount of H$_2$ is more than 20%. The nearly constant total soot volume fractions between 10 to 20% H$_2$ addition can actually be expected from the distributions of the predicted flame cross sectional area integrated soot volume fractions shown in Fig.4(b), where it is seen that the peak value of $F_v$ is almost unchanged and the distribution curve of $F_v$ simply moves slightly downstream when the added amount of H$_2$ is increased from 10 to 20%.

![Fig.5 Comparison of the predicted and measured total soot volume fractions in the coflow CH$_4$ diffusion flame at different levels of H$_2$ and He addition up to 40%.](image)

To gain insights into the different role played by H$_2$ on soot formation when added to CH$_4$ and C$_2$H$_6$, the influence of 20% H$_2$ or He addition to fuel in the CH$_4$ diffusion flame was examined. The radial profiles of the calculated mole concentration of pyrene, which is directly responsible for the soot nucleation process in the present soot model, at three streamwise locations are shown in Fig.6(a). It is noticed that there are two substantial differences in the predicted pyrene concentrations between the CH$_4$ flame and the C$_2$H$_6$ flame [6]. First, the concentration of pyrene decreases significantly with decreasing the streamwise location in the CH$_4$ flame. In the C$_2$H$_6$ flame, however, Guo et al. [6] showed that the peak pyrene concentrations are almost constant in the near burner region between $z = 1$ and 2.9 cm. In addition, the pyrene concentration in the CH$_4$ flame at the early stage of soot formation, $z = 2.8$ cm, is an order of magnitude lower than that in the C$_2$H$_6$ flame. Secondly, the pyrene concentration in the hydrogen diluted flame is higher than that in the helium diluted one in the soot nucleation region, see curves in Fig.6(a) at $z = 2.8$ cm around $r = 0.4$ cm. In contrast, the pyrene concentration in the hydrogen diluted C$_2$H$_6$ flame is lower low in the flame [6].

The radial distributions of the nucleation rate with and without 20% dilatation are shown in Fig.6(b). It is not surprised to see that the nucleation rate in the hydrogen diluted flame is higher than that in the helium diluted one in the early stage of soot formation, due to the higher pyrene concentration. This is again in contrast to that in the C$_2$H$_6$ flame [6].
The different effects of hydrogen and helium addition to CH₄ and C₂H₄ on the concentrations of benzene and pyrene are believed to be the primary reason for the different effectiveness of hydrogen to soot suppression, relative to that of helium, in these two flames. It is worth pointing out that although soot nucleation indeed contributes fairly little to the overall soot yield, it is the initiation and the bottleneck step in the entire soot formation process and plays a vital role in the total soot yield.

The chemical effect of hydrogen on soot suppression in the ethylene flame was identified to be the lower hydrogen atom concentration, which suppresses the H-abstraction rate of the overall HACA surface reaction sequence, in the surface growth regions in the hydrogen diluted C₂H₄ flame [6]. The radial profiles of H model concentration with and without dilution are compared (not shown). These results indicate that the H atom concentrations in the soot nucleation and growth regions are lower in the hydrogen diluted flame, which is in qualitatively agreement with that observed in the C₂H₄ flame [6]. Although the lower H atom concentration was identified to be the primary reason for the chemically inhibiting effect of hydrogen on soot reduction in the C₂H₄ flame [6], it is evident that it is not the case in the CH₄ flame studied here.

4. Conclusions

The experimental and numerical results indicate that addition of hydrogen or helium to methane reduces the soot yield and hydrogen is significantly less effective than helium on soot suppression. This finding is in contrast to the previous studies on the additional chemical effect of hydrogen addition to ethylene on soot suppression. The reason for the less effectiveness of hydrogen addition to methane on soot reduction than helium is that hydrogen addition enhances concentrations of PAHs in the near burner regions, which results in greater soot nucleation and surface growth rates in the early stage of soot formation and ultimately larger amount of soot yield. The present study also demonstrates that the soot model is not robust for the reason that it predicts the soot volume fractions an order of magnitude lower than the experimental data, though it correctly predicts the relative effectiveness of hydrogen and helium addition to methane to soot suppression observed in the experiment.

References