Soot Formation in Strained Diffusion Flames with Gaseous Additives

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The effects of various gaseous additives on soot formation in strained diffusion flames are reported. The additives N₂, Ar, He, H₂, and CO were introduced with fuels C₂H₄, C₃H₈, and C₄H₁₀, and were selected to isolate the effects of dilution, temperature, preferential diffusion, and active chemical participation resulting from the additive. Special emphasis was placed on understanding the mechanisms by which CO and H₂ addition influence soot inception. Measurements were made of the limiting strain rate for complete suppression of soot, i.e., the soot–particle inception limit, Kₛ, in the counterflow diffusion flame. Some laser-extinction measurements of soot volume fraction were also made in the coflow flame to determine the applicability of the results to this geometry. The addition of inert to the fuel decreases the sooting limit due to the reduction in fuel concentration and temperature. Concentration modification due to preferential diffusion enhances the suppressive effect of He, causing it to be the most effective additive considered. The behavior of the reactive additives is more complex. The addition of H₂ increases flame temperature but decreases Kₛ for the fuels considered. Preferential diffusion is partially responsible for this behavior, however direct chemical suppression may also play a role in the strongly suppressive effects of this additive. The chemical role of H₂ is discussed in the context of Frenklach's H abstraction/C₂H₂ addition model for PAH formation. Carbon monoxide addition to C₂H₄ results in a monotonic decrease in Kₛ that is primarily a consequence of dilution. For CO addition to the alkanes there is initially an increase in Kₛ followed by a decrease for X_{CO} > 0.5, suggesting a small chemical enhancement. Coflow results tend to support these findings: For C₂H₄ the results are consistent with dilution while for C₃H₈ a small chemical enhancement combined with suppression due to dilution nets a weak suppression of soot formation. This finding, that CO can enhance inception chemistry in alkanes, requires further study.

INTRODUCTION

Recent studies have revealed that the effects of gaseous fuel additives on soot formation in diffusion flames can be rather complex even when the additive is a simple inert [1–5]. The additive can influence soot formation through its effects on fuel concentration, temperature, residence time and chemistry, and this influence can occur in the inception, growth, and oxidation stages. Furthermore, these effects are strongly coupled such that introduction of the additive affects the soot formation process not only indirectly (passively) through fuel dilution and consequently modification of the temperature field and residence time, but also directly (actively) through participation of the additive in the chemical mechanism.

To further understand the role of fuel additives in soot formation in diffusion flames, we have investigated the effects of CO, Ar, N₂, He, and H₂ as additives to ethylene, propane, and butane. Such a study, which includes reactive species (CO and H₂), highly diffusive species (H₂ and He) and nonreactive, near-equidiffusive species (Ar and N₂), allows comparisons to be made that help to identify the mechanisms by which these additives affect soot inception.

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Specifically, we are interested in identifying the chemical role of H$_2$ and CO in strained diffusion flames. Isolating a chemical effect for a fuel-additive like H$_2$ is complicated by the fact that not only does the introduction of the additive affect the fuel concentration, temperature and residence time, but soot formation will also be influenced by the nonequidiffusive nature of the mixture.

We approach the problem based on the following considerations. First, the effects of the near-equidiffusive additives Ar and N$_2$ are investigated. These additives provide an unambiguous understanding of the effects of fuel dilution and temperature [1, 6]. Next, the effects of helium, a highly mobile additive, are studied. As shown in Ref. 4, a highly mobile additive, characterized by its large diffusivity, can be more effective at suppressing soot formation in positively strained flames than one that is less mobile because the precursor concentrations in the soot region are reduced by the highly mobile additive. Finally, having used the above additives to understand the relative effects of fuel dilution, flame temperature, and preferential diffusion, we can attempt to determine the effects of H$_2$ and CO addition on soot chemistry. For example, H$_2$ is highly mobile and noncarbonaceous; thus, based on the above arguments for dilution and preferential-diffusion, one might expect that H$_2$, is an effective soot-inhibiting additive in positively strained flames. However, H$_2$ addition will also influence the flame temperature and soot chemistry. Thus, to unambiguously identify an active chemical role for H$_2$ we must identify the relative importance of dilution, preferential diffusion and temperature.

No previous studies have been reported on the addition of H$_2$ or CO to the fuel of counterflow diffusion flames. In coflow flames H$_2$ is known to be an effective soot inhibitor [7–9], although the reason for this is not fully understood and the role of preferential diffusion has not been considered.

There is surprisingly little information available for CO as fuel additive in coflow diffusion flames. Arthur and Napier [10] found CO to have a weakly suppressive effect on soot formation in methane flames but did not offer an explanation for this behavior. The addition of CO would be expected to affect fuel concentration and flame temperature, and possibly soot chemistry. To isolate and understand the mechanisms responsible for the behavior of this additive, it is studied in a manner similar to that of H$_2$. However, preferential diffusion is not expected to play a significant role for CO because its diffusivity is comparable to that of the fuels. Therefore, isolating an active chemical role for CO is somewhat simpler and more definitive than for H$_2$.

As noted above, the primary emphasis of this work will be on soot inception. Most of the experiments are performed in a counterflow flame where the strain rate can be easily controlled and characterized. Kennedy [11] and the present authors [5, 6] have demonstrated that for counterflow flames the sooting limit $K_p$, defined as the limiting strain rate for suppression of soot, is useful in identifying a characteristic rate for soot-inception chemistry. Therefore, $K_p$ is used as an indication of how this chemistry is affected by the additive. Line-of-sight measurements of soot volume fraction in a coflow flame are also made as a means of identifying the applicability of the conclusions to alternate flame configurations.

**EXPERIMENTAL**

The experimental apparatus and methodology are identical to those reported previously [5, 6] and will only be described briefly. In the counterflow diffusion flame configuration, a flame is established between two high-contraction nozzles that were designed to yield uniform flow at their outlets. The sooting limit, which corresponds to the particle-inception limit $K_p$, is identified by increasing the strain rate until light scattering due to soot particles is totally suppressed when compared to background scattering due to gases. Appropriate care is taken to ensure that the broadband fluorescence signal has been accounted for [6]. When the critical strain rate for suppression of soot is attained, the velocity on the oxidizer side of the flame is measured by laser doppler velocimetry and $K_p$ is defined as the local velocity gradient upstream of the flame. As defined, $K_p$ yields a characteristic rate for the soot inception chemistry [6].
The coflow burner consists of two concentric tubes with fuel issuing out of a 1.17 cm i.d. inner tube and the oxidizer from a 7.2 cm i.d. outer tube [5]. The flames are overventilated such that increases in oxidizer flow do not influence the flame height. Integrated soot volume fractions can be obtained from laser-light extinction measurements through the centerline of the flame. The line-of-sight measurements yield the line integral of the soot volume fraction $F$, at a given axial position. From Beer’s law,

$$ F = \int_{-\infty}^{+\infty} \phi \, dx = -C(\lambda, \bar{n}) \ln(I/I_0), $$

where $\phi$ is the local soot volume fraction, $I/I_0$ is the transmittance and $C(\lambda, \bar{n})$ is a constant of proportionality equal to $1.29 \times 10^{-5}$ when $\lambda = 632.8$ nm and $\bar{n} = 1.57 - i0.56$. In this work we report only $\ln(I_0/I)$ to avoid uncertainties in the refractive index $\bar{n}$.

Temperature measurements are obtained with a BeO-Yt$_2$O$_3$-coated 20% Rh-Pt/40% Rh-Pt thermocouple (50 µm wire diameter) and are corrected for radiation loss. To obtain the emissivity of the coated bead, temperatures were measured under identical conditions with thermocouples having different bead sizes. An emissivity of 0.38 was found to yield identical radiation-corrected temperatures for different thermocouples. This value is used to be consistent with previous works [5, 6].

A primary goal of this work is to identify dilution, temperature, and chemical effects of the additive. To do this we must isolate the effect of flame temperature. One method of accomplishing this is to first add the additive and then adjust the flame temperature back to the value corresponding to that of the neat fuel flame without changing either the fuel or oxygen concentrations. In this work such a temperature adjustment is accomplished by replacing an appropriate portion of the nitrogen in the oxidizer with argon [1]. In this way, the concentrations of the reactive species are not affected by the temperature adjustment technique. Furthermore, the transport properties of argon and nitrogen are similar enough that the flame location and flame structure in the soot regions are not significantly altered by the inert substitution [1].

**RESULTS AND DISCUSSIONS**

Figures 1–3 show the particle inception limit, $K_p$, as a function of the freestream mole fraction of the additive for ethylene, propane, and butane counterflow diffusion flames. The oxygen mole fraction for the ethylene flame is 18.8% as opposed to 21% for the alkanes, yielding similar flame temperatures for the neat fuel flames.

Since $K_p$ is the critical strain rate at which particle inception is suppressed, a decrease in $K_p$ implies a decrease in the rate of particle-inception chemistry. Figures 1–3 reveal that while there are distinct differences in the ef-

![Graph](https://via.placeholder.com/150)

**Fig. 1.** Effects of $N_2$, CO, Ar, He, and $H_2$ addition to $C_2H_4$ on the soot-particle inception limit $K_p$. $K_p$ characterizes the rate for soot-particle inception chemistry. The oxidizer is 18.8% $O_2/81.2% N_2$. The temperature of the neat $C_2H_4$ flame (indicated by the star symbol) is similar to that of the neat $C_3H_8$ flame in Fig. 2.

![Graph](https://via.placeholder.com/150)

**Fig. 2.** Effects of $N_2$, CO, Ar, He, and $H_2$ addition to $C_3H_8$ on the soot-particle inception limit $K_p$.
fectiveness of the additives, the curves for Ar and N₂, and for H₂ and He display trends that are similar, particularly for the ethylene flame. Carbon monoxide shows a weakly suppressive effect in the ethylene flame until the fuel stream is largely composed of the non-sooty additive. However, the addition of carbon monoxide to the alkanes results in an interesting non-monotonic behavior. For nearly equal molar quantities of alkanes and CO, ͞ is greater than for the neat fuel, despite the nonsooty nature of the additive. Beyond 80% CO, ͞ falls off rapidly, which is reasonable since the chemistry is now dominated by that of the additive.

The temperature of the flame is also changed as a consequence of the introduction of the additive. We will use maximum flame temperature, which is in close proximity to the soot inception zone, to characterize temperature. The temperatures reported were measured at the strain rate corresponding to ͞ for the neat fuel flames. For the soot limit data, the temperatures did not vary appreciably with strain rate at the experimental conditions because the soot-particle inception limit occurs at a much lower strain rate than the strain rate for flame extinction [6]. In other words, ͞ corresponds to a Damköhler number that is large and far from the turning point where extinction occurs.

In Figs. 4 and 5 we have plotted the measured maximum temperature, ͞, against additive mole fraction for C₂H₄ and C₃H₈. For both fuels, the flame temperature is found to generally increase when H₂ and CO are added but decrease when the inerts are added. The flame temperature decreases rapidly when the C₂H₄ flame approaches 100% CO, a result consistent with the weak burning intensity of CO in the absence of sufficient quantities of H₂O. No attempt was made to completely eliminate H₂O from the fuel or oxidizer because of the large amount of fuel-generated H₂O present in hydrocarbon flames; the drop in temperature as the CO mole fraction of the freestream XCO, reaches unity is just an indication of the substantial reduction in H₂O when hydrocarbons are eliminated from the fuel mixture.

Fig. 3. Effects of N₂, CO, Ar, He, and H₂ addition to C₄H₁₀ on the soot-particle inception limit ͞.

Fig. 4. Effects of N₂, CO, Ar, He, and H₂ addition to C₂H₄ on measured flame temperature. The oxidizer is 18.8% O₂/81.2% N₂.

Fig. 5. Effects of N₂, CO, Ar, He, and H₂ addition to C₃H₈ on measured flame temperature.
The results outlined above will now be discussed in greater detail, first for inert addition, then H₂ addition, and finally CO addition.

Inert Addition

Figures 4 and 5 show that with inert addition the extent of temperature reduction increases in the order of Ar, N₂, and He. For Ar addition, the smaller heat capacity compared to that of N₂ causes the flame temperature to be less affected. For He addition, the temperature response is more complex because helium significantly affects the Lewis number of the mixture. Based on heat capacities alone, the temperature reduction with Ar and He addition should be the same; thus the lower flame temperature of the He-diluted flame is due to its larger Le. Broadening of the temperature distribution is expected because of the high rate of thermal transport for helium, particularly when the additive mole fraction is large. The increase in the temperature difference between the Ar- and He-diluted flames with additive mole fraction is consistent with an increase in broadening.

Also shown in Fig. 4 with hatched lines is the inert-additive mole fraction at which flame extinction occurs for K = 150/s. Similar to the results of Ishizuka and Tsuji [12] for methane flames, extinction of C₂H₄ flames occurs at about the same flame temperature when diluted with either Ar or N₂, even though the Ar-diluted flame has a lower fuel concentration. The He-diluted flame, however, extinguishes with a higher temperature and fuel concentration. These extinction conditions occur at fuel concentrations substantially lower than those for soot suppression.

The temperature variations will impact the particle inception limits. To identify the extent to which the variations in K_p are due to changes in temperature, we have, in Figs. 6 and 7, replotted the data of Figs. 1 and 2 against the T_f data of Figs. 4 and 5, respectively. The dashed curves plotted in Figs. 6 and 7 are results that depict the dependence of K_p on T_f alone. The procedure used to obtain the dashed curves is discussed in detail in Ref. 6. Briefly, it involves replacing a portion of the nitrogen in the oxidizer with an equal molar

amount of argon. In this way the flame temperature is varied while the fuel and oxidizer concentrations are held constant. The dashed curves in Figs. 6 and 7 represent K_p ~ exp(-E_a/T), where T is the measured flame temperature and the activation energies were obtained from Arrhenius plots of K_p vs. 1/T [6]. Therefore, the curves represent thermal effects on soot inception. The deviation of the data from the dashed curves indicates that the

Fig. 6. Cross-plot of Figs. 1 and 3 showing the soot particle inception limit versus flame temperature. The dashed curve depicts the purely thermal effect on inception limit and was obtained without changing the fuel or oxygen concentrations. This curve corresponds to a global activation energy of 31 kcal/mol.

Fig. 7. Cross-plot of Figs. 2 and 4 showing the soot particle inception limit versus flame temperature. The dashed curve depicts the purely thermal effect on inception limit and was obtained without changing the fuel or oxygen concentrations. This curve corresponds to a global activation energy of 30 kcal/mol.
additives are influencing particle inception by mechanisms other than flame temperature. The most notable observation for the inert is that the fall off in $K_p$ with inert addition is more rapid than expected from purely thermal effects, suggesting an additional mechanism is involved in suppression.

The effects of nitrogen addition have been shown to be a consequence of a reduction in fuel concentration (dilution) as well as temperature, both of which decrease the soot limit [6]. For argon the situation is much the same; however at a given flame temperature the freestream fuel concentration of the Ar-diluted flame is less than that of the N$_2$-diluted flame and, consequently, $K_p$ should be less as well. While this is clearly the case for the ethylene flame (Fig. 6), for the propane flame (Fig. 7) the results for N$_2$ and Ar are quite similar. This may be due to preferential diffusion because argon is somewhat less mobile than nitrogen and will thus be slightly less effective at suppressing soot than nitrogen, particularly when the inert is added to the fuel of the counterflow flame [4].

The effects of concentration modification due to preferential diffusion are more pronounced for the He-diluted flame. Figures 6 and 7 show that at a given flame temperature $K_p$ is much less for helium than for nitrogen or argon, even though the freestream fuel concentration $X_{F,0}$ is higher (refer to Figs. 1 and 2). For example, to obtain a flame temperature of 1950 K in the ethylene flame, the additive mole fractions were 0.4 for argon, 0.3 for nitrogen, and 0.2 for helium ($X_{F,0} = 0.6, 0.7, \text{and } 0.8$, respectively). Based solely on effects of freestream fuel concentration, one would expect $K_p$ to be greatest for helium addition. In fact it is the least because local concentrations are modified due to preferential diffusion of the more diffuse species [4]. It should be noted that any broadening of the temperature distribution that would result from the large thermal conductivity of helium would lead to a thicker pyrolysis zone for a given maximum temperature and a greater, not lesser, $K_p$. Therefore, any effect of thermal broadening is being overshadowed by preferential diffusion in these flames.

The understandings gained from these inert addition studies, where we have considered highly diffusive as well as diffusively neutral species, facilitates qualitative understanding of the effects of hydrogen addition, to be discussed next.

**Hydrogen Addition**

The role of H$_2$ on soot-inception chemistry in the counterflow diffusion flame depends on not only its effects on flame temperature and hydrocarbon concentrations, but possibly its active chemical participation. Furthermore, hydrogen, like helium, is highly mobile, implying that preferential diffusion is important and that the concentration of this mobile additive will be higher in the soot region than it would be for a less-mobile, though reactive, additive.

As observed in Figs. 1–3, H$_2$ addition leads to a substantial reduction in $K_p$, comparable to that for He addition, despite the fact that the measured flame temperature increases with H$_2$ addition. If the additive does not participate in the soot chemistry—effectively behaving as an inert—then the results could be explained as follows: the effects of the higher temperature of the hydrogen flame, which cause the flame to have a greater propensity to soot, are being offset by the effects of preferential diffusion, which cause $K_p$ to be less.

Molecular hydrogen, however, is not expected to behave as an inert with respect to soot inception. Frenklach [13] has proposed the H-abstraction/C$_2$H$_2$-addition reaction mechanism for polycyclic aromatic hydrocarbon (PAH) growth and discussed three possible regimes wherein the role of H$_2$ varies: (I) the “high-temperature” regime where [H$_2$] is greater than or comparable to [C$_2$H$_2$]; (II) a low temperature regime where [C$_2$H$_2$] $\gg$ [H$_2$]; and (III) a low temperature regime where [C$_2$H$_2$] $\ll$ [H$_2$]. Frenklach argues that different parameters control the growth of PAH for these three conditions. Which, if any, of these regimes are applicable to the present diffusion flame can be assessed by considering the results in Ref. 14 where concentration profiles were experimentally obtained for C$_2$H$_8$ flames and numerically obtained for C$_2$H$_4$ flames. From these results it can be inferred that regime I is applicable in the high temperature
region close to the flame, while regime III is more applicable to the cooler regions of the flame, closer to the fuel tube where the C₂H₂ concentration has fallen off but the H₂ concentration is still high, presumably due to back diffusion.

Frenklach's model shows that for regimes I and III, PAH growth rates vary with [H]/[H₂], where the inverse dependence on [H₂] is due to the reverse reaction for H-abstraction

\[ A_i + H \rightleftharpoons A_i^- + H_2. \]  

Here \( A_i \) denotes an aromatic molecule containing \( i \) aromatic rings and \( A_i^- \) denotes an aromatic radical. Now [11] contributed by the additive should be first order or less in [H₂] so the finding that \( K_p \) decreases with H₂ addition, even though the temperature increases, could be due, in part, to the direct chemical influence of molecular hydrogen. Indeed, shock tube studies of acetylene pyrolysis [15, 16] show that H₂ addition substantially reduces soot formation, as anticipated by this model [16].

Though chemical suppression of soot in diffusion flames due to addition of H₂ to the fuel seems likely, the reduction in \( K_p \) is also a consequence of reductions in freestream fuel concentration (fuel dilution) and local hydrocarbon concentration through preferential diffusion. The complexity of this process precludes an adequate experimental isolation of these effects and an evaluation of individual roles. Thus this study must remain inconclusive as to the exact process by which H₂ suppresses soot inception in the counterflow diffusion flame.

**Carbon Monoxide Addition**

The addition of CO to C₂H₄ yields a monotonically decreasing \( K_p \) (Fig. 1). To determine whether CO addition influences inception chemistry, the data from Fig. 1 is plotted in Fig. 8 against those for N₂ addition, where the temperature of the N₂-diluted flame was maintained constant at that of the neat-fuel flame by substituting a portion of the oxidizer-nitrogen with an equal molar quantity of argon. Under these conditions the curve for N₂ addition at constant temperature represents the effects of dilution alone. Since the temperature of the CO diluted flame has increased at most 30°C (see Fig. 4), the two curves have almost equal flame temperatures. Furthermore, since the mobilities of N₂ and CO are similar, diffusive effects are similar. Thus the similarity of the two curves suggests that the reduction in \( K_p \) with CO addition in the C₂H₄ flame is largely due to fuel dilution. The curve for \( K_p \) does not fall off as quickly for CO, possibly due to the small increase in flame temperature.

As noted previously, CO addition to C₃H₈ and C₄H₁₀ yields a weak and non-monotonic dependence for \( K_p \) (Figs. 2 and 3). The initial increase in \( K_p \) with CO addition may be partially due to the increase in temperature. However, as is evident from Fig. 7, the increase is too large to be totally a thermal effect because the Arrhenius curve, which indicates purely thermal effects, falls well below the data.

The trends observed for soot inception rate should be manifest in soot yield because of the strong influence of inception on soot production rates. Therefore, before discussing possible reasons for the effects of CO addition, we will consider light-extinction measurements of integrated soot volume fraction in coflow flames. To be consistent with previous studies [5, 6], the flow rates of the fuels are kept
constant at 3.0 sccs for ethylene and 2.0 sccs for propane. Thus, for each fuel the flame dimensions do not change appreciably with CO addition [17], particularly since the flame temperature of the CO-diluted flames differed by less than 50°C in the range considered. With temperatures and dimensions being similar, the axial position \( z \) corresponds to a common residence time for all flames of a particular fuel. Therefore, the rate of change of the line-of-sight integrated soot volume fraction, \( F_v = \frac{\ln(I/I_0)}{z} \), in the soot growth region is used as an indicator of the soot formation rate, defined as the change in soot volume fraction with time.

Figures 9 and 10, respectively, show the axial profiles of \( \ln(I_0/I) \) for ethylene and propane flames with CO addition to the fuel when the oxidizer is air. The common shape of the curves is known to be a consequence of soot growth for approximately the first half of the curve followed by soot oxidation for the latter half. Then for comparison with the \( K_p \) data, which is not affected by soot oxidation, the region of importance is the lower region of the flame (small \( z \)) up to the region where \( \ln(I_0/I) \) is a maximum.

The ethylene coflow-flame data in Fig. 9 yields the same basic trends as the counterflow data in Fig. 1 where the sooting tendency consistently decreases with CO addition. For the propane flame (Fig. 10), \( \ln(I_0/I) \) also decreases monotonically with \( X_{CO,0} \), but the reduction is substantially less than for the ethylene flame.

It is clear from Figs. 9 and 10 that the maximum integrated soot volume fraction \( F_{v,\max} \) is indicative of the growth rate in the soot growth region. Thus, in Fig. 11 we have plotted \( F_{v,\max} \) normalized by its value for the neat fuel flame as a function of freestream fuel mole fraction \( X_{F,0} \). The data for \( C_2H_4 \)-reveal a linear dependence of \( F_{v,\max} \) on \( X_{F,0} \) for CO addition. This result is consistent with Fig. 8, which identified a purely dilution effect for CO addition, because earlier coflow flame studies by the authors [18] and Gulder and Snelling [19] have shown that fuel-dilution (at constant

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**Fig. 9.** Profiles of \( \ln(I_0/I) \) for coflow flames with CO addition to ethylene. The ethylene flow rate is constant and equal to 3.0 sccs. Integrated soot volume fraction is proportional to \( \ln(I_0/I) \).

**Fig. 10.** Profiles of \( \ln(I_0/I) \) for coflow flames with CO addition to propane. The propane flow rate is constant and equal to 2.0 sccs. Integrated soot volume fraction is proportional to \( \ln(I_0/I) \).

**Fig. 11.** Effects of CO addition to \( C_2H_4 \) and \( C_3H_8 \) on normalized maximum integrated soot volume fraction in coflow diffusion flames with constant fuel flow rates. Data are extracted from Figs. 9 and 10.
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temperature) yields a linear dependence of \(F_{\text{in}, \text{max}}\) on \(X_{F,0}\).

The gradual reduction in \(F_h\) with CO addition to \(C_3H_8\) suggests a more complicated behavior for this fuel because if CO was acting as an inert the curve in Fig. 11 would be similar to that of \(C_2H_4\). These results, combined with the results from inception limit data for \(C_3H_8\) in Fig. 2 and \(C_4H_{10}\) in Fig. 3, imply that CO is acting to accelerate soot chemistry for these fuels, although the effect is rather weak. Arthur and Napier \[10\] measured the fuel flow rate for suppression of luminosity in methane coflow diffusion flames and they also observed that CO is weakly effective at suppressing soot, much less effective than \(N_2\) addition. These results suggest that CO addition yields a small but observable enhancement in soot chemistry for the alkanes.

Carbon monoxide could influence the radical pool through, for example,

\[
CO + OH \rightarrow CO_2 + H. \tag{3}
\]

This reaction, if it occurs in the soot inception zone, would enhance soot formation for two reasons: First, it depletes the hydroxyl radical concentration and thus the oxidative attack of OH on soot precursors; second, it supplies additional H radicals to the fuel pyrolysis zone which will increase the radical attack on the fuel molecules and promote PAH formation \[13\].

For CO addition to the fuel to affect reaction 3 there must be an increase in the amount of CO in the region where the fuel-side OH concentration is appreciable (i.e., the edge of the particle inception zone \(x_i\)) \[20\]. In this region the amount of flame-generated CO is large, making it difficult to be definitive about the impact of CO addition on the local CO concentration. An estimate of the increase in available CO near \(x_i\) can be obtained from experimental data in Ref. 14. In that work, concentration profiles were measured in a 20\% Ar/80\% \(C_3H_8\) counterflow diffusion flame. Although CO is not a conserved scalar, the amount of Ar in this flame is indicative of the amount of additive-CO that is available to react in the CO/\(C_3H_8\) flame. The data indicate that under similar conditions there would be in the neighborhood of 30\% more CO available in the region of \(x_i\). This additional CO could affect the OH and H concentrations and consequently the soot inception rate. Based on this reasoning, however, it is not clear why the added CO appears to behave as an inert in the \(C_2H_4\) flame.

It should be noted that recent shock-tube studies have revealed that CO addition can lead to a strong enhancement of soot during low-pressure pyrolysis of benzene \[21\]. This finding allows for the possibility that CO can enhance soot formation in diffusion flames by affecting the pyrolysis chemistry. If so, this could account for the fuel specific behavior of the additive in the present study. The mechanism by which this might occur will require further study.

CONCLUSIONS

The soot-particle inception limit has been employed to identify the processes affecting soot inception when various gaseous additives are introduced with the fuel. The effect of the inert additives, \(N_2\), Ar, and He, is qualitatively similar to previous findings for soot formation rates. Preferential diffusion plays a significant role for He addition, causing it to be the most effective additive tested for inhibiting soot inception. The importance of preferential diffusion in these studies suggests that, in general, its implications should be evaluated when considering additives with very large or small diffusivities. For example, hydrogen, with its large diffusivity, should be quite effective at suppressing soot inception in strained flames. Our results show that it is, despite a corresponding increase in flame temperature. Further work, however, must be performed to determine to what extent the results are due to preferential diffusion or chemical suppression. Carbon monoxide addition to the alkanes yields a slight enhancement in soot chemistry as measured by the particle inception limit in counterflow flames and laser extinction in coflow flames. This observation has apparently not been reported previously and deserves further study because it implies that flame-generated CO could also be affecting soot-inception chemistry.
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