PREFERENTIAL DIFFUSION AND CONCENTRATION MODIFICATION IN SOOTING COUNTERFLOW DIFFUSION FLAMES

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An experimental investigation has been conducted on the influence of the mobility of inert additives on soot formation in propane and ethylene counterflow diffusion flames. Inerts used were helium, neon, argon, or krypton, and the results show that while the mobility of the inert has practically no effect when a small amount of inert is added to the oxidizer side, the influence is significant when added to the fuel side in that krypton, being the least mobile inert, yields the greatest soot loading while helium, being the most mobile, yields the least. By relating the spatially-resolved soot volume fractions to the corresponding profiles of temperature, velocity and species concentrations, it is demonstrated that this influence on soot loading is likely caused by concentration modifications of the fuel and the soot precursors due to the different mobilities of the inert additives.

Introduction

Flame phenomena are strongly influenced by the diffusive processes of the reactants. Since the diffusivities of the various species in a gaseous mixture are in general not equal, it is reasonable to expect that the local reactant concentration will be dependent on the extent to which the diffusivities differ. This concentration modification through preferential diffusion can in turn affect the flame behavior from that anticipated based on the freestream concentrations. Indeed, there exist many flame phenomena which can only be satisfactorily explained on the basis of preferential diffusion. For premixed flames, we cite the earlier works of Refs. 1 and 2 and the recent advances as summarized in Ref. 3. The amount of research on nonpremixed flames, however, has been less; some recent contributions include analyses and experiments on flame extinction.

The objective of the present work is to study the effect of preferential diffusion and thereby concentration modification on an important nonpremixed flame phenomenon in which diffusive transport and chemical kinetic processes are inherently coupled, namely soot formation when inerts of different diffusivities are added to either the fuel or the oxidizer stream.

That diffusional stratification may influence the soot formation process can be demonstrated by the following experimental anomaly: In his study of the influence of the various diluents on the soot formation process, McLintock varied the inert diluent on the oxidizer side of an ethylene colllow flame and found that the smoke points decreased in the order of helium, nitrogen and argon. That is, the propensity to soot was least when the oxidizer diluent was helium and greatest when the diluent was argon. With the heat capacities of argon and helium being the same, it was reasoned that the difference was due to the high diffusivity of helium, causing the concentration of helium to be greater within the flame.

An opposite result, however, was reported by Schug et al., who found that when helium was added to the fuel side of an ethylene colllow diffusion flame, it was not as effective as argon in suppressing soot. In fact, helium was the least effective additive for soot suppression. This behavior was attributed to helium’s high thermal diffusivity and its subsequent effect on the temperature distribution and thereby the fuel pyrolysis rate.

While Refs. 7 and 8 have respectively used concentration modification and temperature modification...
tion to interpret the different trends of their results, it is of interest to note that these observations can also be explained, in a consistent manner, as a consequence of either concentration modification or temperature modification alone. For example, by using the temperature modification interpretation, the difference in the results for helium could be solely a consequence of the broadening of the temperature distribution due to helium. That is, when helium is added to the oxidizer side, the broadened temperature distribution has a greater influence on the rate of particle burnup and a lesser influence on the rate of soot formation, implying that helium would be an effective soot suppressor relative to argon. On the other hand when helium is added to the fuel side, the temperature broadening would promote the soot formation rate but not the burn-up rate, implying that helium would be less effective in suppressing soot.

We next adopt the alternate viewpoint that concentration modification could be the physical mechanism responsible for the anomalous results for helium. Recognizing that helium is more mobile than argon, it is clear that when the inerts are added to the fuel, helium will be defocused to a greater extent than argon due to the compressive, concave curvature of the co-flow flame. Consequently, in all but the lowest regions of the flame, the fuel concentration of the helium-diluted mixture will be higher than that of the argon-diluted mixture, implying that the former has a greater propensity to soot. By applying the same reasoning to the oxidizer side, and recognizing that helium is now focused to a greater extent due to the convex flame curvature, the fuel concentration with the helium-diluted oxidizer will be relatively lower, implying that the propensity to soot is reduced.

In order to further understand the relative influences of temperature modification versus concentration modification on the soot formation process, we have adopted an entirely different flame configuration to study the soot response to inert addition. The flame configuration is that of the counterflow diffusion flame. The rationale for such a choice is that in this flame/flow configuration the effect of concentration modification is opposite to that of temperature broadening, thus allowing unambiguous conclusions to be drawn regarding the effect of preferential diffusion. We shall amplify on this point later in the discussion of the experimental results.

In the next section the experimental methodology and arrangement will be specified. This is followed by presentation and discussion of the experimental results.

Experimental Specifications

In this study the counterflow diffusion flame established in the forward stagnation region of a porous cylinder has been used. The flame is amenable to light scattering and extinction measurements and does not suffer from the complication of oxidizer entrainment at the rim as with jet (co-flow) flames. Measurements are taken along the forward stagnation streamline, which is a line of symmetry.

The burner apparatus is similar to that used by Vandakrahger et al. and has been described in detail in an earlier work. Briefly, it consists of a porous cylinder mounted horizontally in a vertically oriented wind tunnel that has a uniform velocity profile across its test section. The cylinder is mounted to a vertical translator which allows it to be moved in the streamwise direction. The oxidizer gas is supplied by the wind tunnel while the fuel gas is ejected from the porous cylinder. The cylinder is composed of a sintered stainless steel tube with an outside diameter of 2.5 cm, a length of 8 cm, and is cooled uniformly along its axis.

The fuels used are commercial grade ethylene and instrument grade propane. The inerts used are krypton, argon, neon and helium.

Temperature measurements are obtained with silica-coated Pt/Pt-12%Rh thermocouples. The wire diameters used are 0.076 mm for the diluted-propane flames and 0.127 mm for the diluted-ethylene flames as well as flames where the composition of the oxidizer inert is varied. The smaller thermocouple is preferred because it offers less disturbance to the flame and less measurement error due to radiation loss. However, the temperatures in these latter flames are high enough that the thinner thermocouple would melt, thus necessitating the use of the thicker thermocouple.

Soot measurements are obtained by using standard light scattering and extinction techniques with an apparatus and procedure identical to those of Flower and Bowman and described in greater detail in Ref. 11. Soot volume fraction is obtained from the Lambert-Beer law for light extinction with the assumption that the soot particles behave as spherical Rayleigh scatterers and have a complex refractive index of \( n = 1.57-i0.56 \). The soot volume fraction is assumed uniform over the length of the burner, with no correction for end effects. Since this work is concerned with relative changes instead of absolute values, the Rayleigh assumption is acceptable.

Gas sampling of the stable species is performed with an uncooled, quartz microprobe designed with the criterion of Fristrom and Westenberg. To allow for sampling in the sooting region of the flame a probe was designed with an internal plunger that allows soot build-up at the probe orifice to be removed periodically. The orifice diameter is 70 \( \mu m \), and, to ensure that reactions are quenched, sampling is conducted at pressures such that the flow through the orifice is choked. The gas samples are obtained by batch sampling into evacuated vessels and the gas analysis is performed by quantitative mass spectrometry. All data are reported on a dry basis.

A standard flame photometer and velocity components of the streamlines were used for light scattering and extinction measurements, respectively. To increase the oxygen supply to the flame, the oxygen supply was increased from 0.25 to 0.40. Ethylene and oxygen were supplied by a diffusion burner.
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mass spectrometry. Since batch sampling is used, data are not available for water and results are reported on a dry basis.

A standard single-component, laser-Doppler velocimetry (LDV) system is used to measure the velocity component along the forward stagnation streamline. Measurements are made in the forward scattering mode, without frequency shifting. Aluminum-oxide seed particles of 0.05 μm nominal diameter are supplied on the oxidizer side.

The soot loading of the propane diffusion flame in air is too low to measure extinction accurately. To increase the soot loading of propane flames the oxygen volume fraction in the oxidizer is increased from 0.21 to 0.25, with the balance being nitrogen. Ethylene flames do not require enrichment and their oxygen concentrations are maintained at that of air.

For the experimental conditions in this study the flame location is a few millimeters on the oxidizer side of the stagnation point (Fig. 1). The soot formation and growth region lies between the flame and the region of the stagnation point. A consequence of this is that it is the flow field on the oxidizer side that is of primary importance for residence time considerations. Therefore, the upstream velocity of the oxidizer is maintained at 38 cm/s for all studies.

An additional consideration is the gas flow ejected from the burner. Two approaches are used in this study. One is to maintain the volumetric flow rate of the fuel constant. In this case the addition of gas to the fuel increases the ejection velocity from the burner. The other approach is to maintain the fuel ejection parameter constant. The fuel ejection parameter defined for variable gas density is 

\[ f_e = \left( \frac{\rho_0 v_e}{\rho_0 v_0} \right)^{1/2} \]

where \( \rho_0 \) and \( v_0 \) are the gas density and velocity at the burner surface, \( \rho_0 \) and \( v_0 \) the freestream values of density and kinematic viscosity for the oxidizer, and \( \kappa \) the characteristic velocity gradient defined as \( \kappa = 2U_e/R \), with \( U_e \) being the freestream velocity of the oxidizer and \( R \) the burner radius. The fuel ejection parameter defined in this way allows flow similarity to be maintained even when variable density inert gases are added. Only results for constant fuel ejection parameter, \( f_e = -3.0 \), will be presented herein because maintaining flow similarity allows for an interpretation based on distance from the burner. It is of interest to note that the results found to be independent of whether flow rate or fuel ejection parameter is held constant.

Results and Discussions

As discussed in the Introduction, both concentration modification and temperature broadening will yield similar trends for inert addition to the coflow flame. Therefore it is difficult to determine with the coflow flame which, if either, mechanism is the dominant cause for the observed trends. This is not the case with the counterflow diffusion flame. By referencing Fig. 1 it can be seen that the fuel reaches the flame by diffusing across the stagnation plane into the oxidizer side. The streamlines on both the fuel and oxidizer sides of the stagnation plane are such that lighter species, which can more easily diffuse across the streamlines, will preferentially accumulate in the region of the stagnation streamline, while heavier species will be preferentially swept away. Consequently, when helium is added to the fuel, concentration modification should lead to a reduction in fuel concentration and, thereby, a corresponding reduction in the soot loading as compared to the situation of adding argon to the fuel.

We further note that soot burn-up does not occur in the forward stagnation region of the counterflow diffusion flame. Therefore, if helium addition were to broaden the temperature distribution, the effect would be to increase the soot loading as based on the reasoning of Ref. 3 discussed in the Introduction. Thus, in the counterflow diffusion flame, the effect of concentration modification is opposite to that of broadening of the temperature distribution and we can compare the relative importance of the two mechanisms for this flame.

In addition to helium and argon we have also used neon and krypton for diluents in this study. All diluents are therefore completely inert and since they are monatomic and have the same heat capacity, they should have a similar influence on the maximum flame temperature.

The soot volume fraction drops off around the
stagnation point because of the inability of the soot particles to propagate past the stagnation point into the fuel side (see Fig. 1). Data in this region have been suppressed as they are not relevant to this work.

The soot volume fraction distributions along the stagnation streamline for the propane/inert mixtures are plotted in Fig. 2. The curves show a strong relationship between the mobility of the inert and the maximum soot loading for the flame. Krypton, being the least mobile inert, yields the greatest soot loading \(0.52 \times 10^{-5}\) while helium, being the most mobile, yields the lowest soot loading \(0.26 \times 10^{-5}\).

The results for inert addition to ethylene, shown in Fig. 3, display trends similar to those of the propane flames in both their relationship to the inert mobility and in the extent of the change in soot volume fraction; the soot loading increases with decreasing inert mobility, and the maximum soot volume fraction of the krypton-diluted flame is about twice as high as that of the helium-diluted flame.

The above results indicate that the soot loading varies with the mobility of the inert added. To determine whether the primary cause for the change in the soot loading is indeed modification of the fuel concentration, we have determined the temperature, velocity, and species concentration profiles for these flames.

Figure 4 shows the temperature distributions, uncorrected for radiation losses, for the propane/inert mixtures. The oxygen concentration for the temperature measurements is that of air, or 21 percent by volume, as compared to 25 percent for the soot volume fraction measurements. While the trends in maximum temperature and temperature distribution will not be affected by the lower oxygen concentration, the soot loading is much reduced. Consequently, the accuracy and reproducibility of the measurements are greatly improved due to the fact that soot build-up on the thermocouple is less.

The maximum flame temperatures measured show slight increases with decreases in the mobility (increases in the molecular weight) of the inert; krypton yields the highest temperature (1641°C), helium the lowest (1511°C). The temperatures for the other inert gases lie in between.

One may note the difference in temperature seen in Fig. 4. This is the influence in the temperature distribution of the flame being unreactive since it is made up of ethylene. The results clearly show the influence in the maximum soot loading increment.

For the ethylene flames, the flame temperature is found to be within 100°C of 2000°C; it is reasonable to assume that the four inert gases used have only a small effect on the flame temperature.

We now consider the velocity effects and their consequences. Since the flames are nominally stagnation point, it is expected that the influences of the velocity are minimal. Figure 5 is a plot of the velocity streamline for the fuel side for the propane/inert flames. The velocity profiles are reasonable; the most identified dynamic similarity is the jet ejection pattern,
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A close inspection of Figs. 2–5 reveals that the locations of the flame and stagnation point are shifted away from the burner surface as the mobility of the inert is increased. The shift in stagnation point is most accurately indicated by the locations of maximum soot in Figs. 2 and 3 while the shift in flame location is indicated by both peak temperatures and velocities in Figs. 4 and 5. The shifts are small (<1/2 mm) and will not influence soot particle residence times because the flame and stagnation point shift together.

This shift can be understood by considering the fact that in these experiments we have maintained \( f_u \) and \( \kappa \) fixed so that, in the nonreactive limit, the flow fields are similar in terms of \( \eta = (\kappa/\rho \mu_u)^{1/2} \)

\[ fgaly. \] Therefore, while the stagnation points occur at the same \( \eta \) for all flows, they are shifted in the physical coordinate \( y \). For example, since the density is less in the helium-diluted flame, the physical distance to the stagnation point is greater. Estimates using mean densities show agreement between the anticipated and observed shifts.

With the velocity and temperature fields being largely independent of the additive mobility, the implication is that the local concentrations of the reactive species have been modified. To verify this, a measurement of the species concentrations within the sooting flames is obtained. Probe sampling of the stable species is performed at conditions similar to those of the temperature measurements, in that the oxidizer is 21 percent oxygen as compared to 25 percent used for the soot data. The lower oxidizer concentration reduces the extent of sooting while preserving the important concentration features.

Fig. 5. Velocity as a function of distance from the burner surface for propane/enriched air (25% \( O_2 \)) counterflow diffusion flames with inert addition on the fuel side.

Fig. 6. Mole fraction profiles of inert diluent (helium and argon) in propane/air counterflow diffusion flames with inert addition on the fuel side.
distance from the burner because concentration gradients in the flame region are steep and the flame locations are not precisely the same. In Fig. 7 the mole fraction of the parent fuel, propane, is plotted as a function of distance from the flame. Near the flame, the concentration gradients are found to be less for the helium-diluted flame which, in itself, delineates that the mole fraction of the fuel will be locally less, and Fig. 7 illustrates this. However, a caveat is necessary with regard to interpreting Fig. 7. The concentration gradients are so steep near the flame that spatial measurement errors of just 0.1 mm could influence the conclusions drawn. Although care was exercised to maximize the spatial accuracy, there is an alternative means of demonstrating the effects of preferential diffusion that is not as sensitive to spatial accuracy.

Concentration modification of the fuel will necessarily lead to a modification of the concentrations of the fuel-based species in the flame and these species will attain a maximum somewhere within the flame. The maximum is insensitive to location and, where applicable, is a good indicator of the relative availability of soot precursors. Table I lists the maximum mole fractions for all measured species except for ethane and propadiene which did not display obvious maxima. Without exception, the mole fractions are higher in the argon-diluted flame, and, in the case of potentially important soot-particle precursors, notably butadiene (diacetylene), butadiene and benzene, the mole fractions are 15-25% higher. The results demonstrate that the local composition is indeed modified in the presence of preferential diffusion and this modification can influence soot formation.

**TABLE I**

<table>
<thead>
<tr>
<th>Fuel Mixture</th>
<th>Hydrogen (H₂)</th>
<th>Carbon Monoxide (CO)</th>
<th>Carbon Dioxide (CO₂)</th>
<th>Methane (CH₄)</th>
<th>Acetylene (C₂H₂)</th>
<th>Ethylene (C₂H₄)</th>
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<tr>
<td>20% He/80% C₃H₈</td>
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<td>.052</td>
<td>.086</td>
<td>.017</td>
<td>.018</td>
<td>.030</td>
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<tr>
<td>20% Ar/80% C₃H₈</td>
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<td>.057</td>
<td>.091</td>
<td>.018</td>
<td>.020</td>
<td>.032</td>
</tr>
<tr>
<td>% Difference</td>
<td>10</td>
<td>9</td>
<td>6</td>
<td>6</td>
<td>10</td>
<td>6</td>
</tr>
</tbody>
</table>

**TABLE I**

<table>
<thead>
<tr>
<th>Fuel Mixture</th>
<th>Propene (C₃H₄)</th>
<th>1-3 Butadiene (C₃H₄)</th>
<th>1-3 Butadiene (C₃H₄)</th>
<th>2-Badene (C₃H₄)</th>
<th>Cyclopentadiene (C₅H₈)</th>
<th>Benzene (C₆H₆)</th>
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<tr>
<td>20% He/80% C₃H₈</td>
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<td>.00042</td>
<td>.00066</td>
<td>.00063</td>
<td>.00021</td>
<td>.000048</td>
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<tr>
<td>20% Ar/80% C₃H₈</td>
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<td>.00049</td>
<td>.00089</td>
<td>.00088</td>
<td>.00024</td>
<td>.000060</td>
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<tr>
<td>% Difference</td>
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<td>14</td>
<td>26</td>
<td>7</td>
<td>12</td>
<td>20</td>
</tr>
</tbody>
</table>
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It may appear somewhat surprising that the stratification of the inert concentrations would affect the composition without affecting the temperature distributions. Although the thermal diffusivities of the inerts used vary widely, these additives are only a small portion of the total gas composition in the region of the flame. Consequently, the thermal transport properties are still dominated by the major species, e.g. nitrogen. The fuel concentration, however, is coupled to the inert concentration so that stratification of the inert can have a significant effect on the concentrations of fuel-related species.

The effects of inert mobility on the oxidizer side of a propane flame are considered in Figs. 8 and 9. Twenty percent of the nitrogen in the oxidizer is replaced with either argon or helium so that the concentration of these test inerts in the oxidizer is 15 percent. Figure 8 reveals that the maximum temperatures of the helium- and argon-diluted flames are still quite similar even though the helium-diluted flame shows some broadening of the temperature distribution. Furthermore, the maximum soot volume fractions seen in Fig. 9 are almost identical. Referring to Fig. 1 it is seen that the transport of fuel from the stagnation point to the flame is totally dependent on diffusion while the transport of the oxidizer to the flame is assisted by convection. Therefore it is reasonable that the mobility of the inert added to the fuel would have a strong influence on fuel concentrations while adding the same inert to the oxidizer side would have little effect on fuel concentrations.

Concluding Remarks

In the present investigation we have provided experimental evidence that gives strong support to the concept that soot formation in diffusion flames can be significantly affected by concentration modification due to preferential diffusion of the reactive/inert species. We have further shown that, while this result is reasonable and possibly not unexpected, a convincing demonstration of this fact requires careful consideration and ultimately elimination of other possible causes, such as those due to the potential modification of the temperature and velocity fields.

Recognizing the existence and importance of diffusional stratification of the concentrations of the reactive mixtures, it would be of interest to extend the present investigation to diffusion flames of other configurations, to premixed flames, and to the formation of other pollutant species which are sensitive to concentration modifications.

Acknowledgments

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REFERENCES

3. Law, C. K.: Dynamics of Stretched Flames, this Symposium.

COMMENTS

R. J. Santoro, Pennsylvania State Univ., USA. In the presentation, you indicated that the temperature was held constant to within about 40 K. Could the variation in temperature account for the small changes (approximately 20%) you observed in the species concentration?

Author's Reply. The concentration modification resulting from preferential diffusion influences flame temperature, and any difference in temperature could, in turn, affect the concentrations of the pyrolysis products. For the helium- and argon-diluted flames the measured difference in maximum temperature is 30°C and a similar temperature difference is found throughout the pyrolysis region. (Note that if there was a noticeable broadening of the temperature distribution due to helium addition, the temperature difference of the two flames would have been even less in the pyrolysis region.)

This difference in temperature certainly plays a role in the concentration differences, however we do not believe that temperature alone can account for the measured differences in either soot or species concentrations. While the authors are not aware of any data describing how flame temperature influences species concentrations for this flame, some insight can be gained by considering results where the influence of temperature on soot concentration of a propane flame was studied. When flame temperature was increased 43°C without changing either the fuel or oxidizer concentration, the maximum soot concentration increased only 13%, far less than the almost 60% increase observed between the helium- and argon-diluted flames of the present study. The variation in species concentrations resulting from a 30°C increase in temperature would not appear to account for the observed variations in soot concentration.

The species measurements shown in Table 1 and Fig. 7 also imply that factors other than temperature are responsible for the measured differences. Not only are the products and by-products of the fuel greater in the argon-diluted flame, the parent fuel concentration is also locally greater—an unlikely result if temperature is responsible for the concentration differences.

REFERENCES