

The Effect of Temperature on the Sooting Behavior of Laminar Diffusion Flames

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Abstract—The effect of temperature on soot formation in a laminar propane diffusion flame was investigated. The temperature of the flame on a Parker Wolfhard burner was varied by adjusting the inert nitrogen content in the oxidizer flow. Local soot aggregate properties, such as aggregate diameters and their number densities as well as soot volume fractions were determined using simultaneous laser light scattering and extinction methods, while spherule diameters were obtained using sample extraction and transmission electron microscopy. Soot volume fractions and aggregate diameters were seen to increase with height above the burner, while the opposite trend was noted for aggregate number densities for the three flame temperatures investigated. Spherule diameters were seen to increase with height particularly in the early part of the flame. An increase in temperature resulted in a considerable increase in local soot volume fractions and aggregate diameters. Spherule size and degree of agglomeration also varied somewhat with temperature. Soot aggregate number densities, at least in the regions of noticeable soot loading, were found to be largely insensitive to changes in temperature. Heights above the burner were converted to residence times in the flame allowing for buoyancy. The mean rate of growth of the largest soot aggregates was found to be essentially independent of flame temperature, although the absolute soot particle diameters were larger in the hotter flames, resulting in an increase in sooting with temperature. An "effective growth residence time" was introduced to take account of the effects of temperature such that both total soot loadings and maximum soot diameter were the same for any given normalized time for all flame temperatures investigated.

I INTRODUCTION

The formation of soot during the combustion of hydrocarbons has become a matter of increasing concern over the last decade. Smoke has been recognized as the major cause of fatalities in building fires [see Neville (1972)] and as a source of atmospheric pollution generated by many practical combustion devices. Furthermore, the increased wall heating due to radiative heat transfer from the solid soot particles results in materials design problems in many combustors. With this in mind a great number of studies have been undertaken to further the understanding of the mechanisms responsible for the formation of soot under a variety of different combustion conditions. A number of excellent review papers have recently been published covering many aspects of the soot formation problem including Wagner (1981), Haynes and Wagner (1981), Lahaye and Prado (1978), Palmer and Cullis (1965), Homan (1967), Howard and Kausch (1980), and Calcote (1981). Since all building fires and many controlled combustion processes occur, at least partially, in the form of diffusion

flames, it was decided to further study the effect of various parameters on the formation of soot in laminar diffusion flames.

Glassman (1979), in a review of phenomenological models of soot formation, addressed the differences in the dependence of sooting behavior on temperature between premixed and diffusion flames. He reported that while for premixed flames an increase in flame temperature will result in a decrease in sooting tendency, a similar rise in temperature in diffusion flames will tend to increase the likelihood of soot being formed. These results were obtained using the concept of sooting height [see also Glassman and Yaccarino (1981)]. Similar observations in laminar diffusion flames were made by Dearden and Long (1968) who report an increased amount of soot collected with increasing flame temperature. This also sheds new light on results reported by Powell *et al.* (1979) on the effect of temperature on the sooting history of flames on wood and PVC. Here, post flame soot loadings and particle diameters were seen to increase with temperature when determined optically in the flue above their test chamber.

Glassman (1979) explained the differences in sooting trends with temperature in premixed and diffusion flames in terms of competing pyrolysis and oxidation reactions in the pre-sooting zones. In premixed flames, the rate of oxidation of soot precursors is accelerated more strongly by an increase in temperature than their formation via the pyrolysis reaction, leading to a reduction in soot. In diffusion flames, on the other hand, no oxidation takes place during preheating leaving only the pyrolysis reactions, which leads to an increase in sooting with temperature. Indeed, traces of oxygen which may diffuse into the pyrolysis zone of a diffusion flame tend to act as a homogeneous catalyst during pyrolysis and increase the sooting rate as was shown by Glassman and Yaccarino (1980) and Schug *et al.* (1980).

All the above observations were made in terms of global measurements such as sooting heights, amount of soot collected, etc. It would be interesting to extend these measurements to determine the effect of temperature on the properties of the soot particles as they are formed inside both premixed and diffusion flames. Soot consists of essentially spherical particles, or spherules, which agglomerate to form the soot agglomerates commonly observed in most flames. The local soot parameters in the flame, which would be of interest, are soot loadings, agglomerate number densities, agglomerate diameters, spherule diameters and, thus, degrees of agglomeration.

Prado *et al.* (1981) have investigated the effect of temperature on the process of soot formation in a propane-air premixed flame [see also Prado and Lahaye (1981)]. They found that for a given fuel air ratio the local soot volume fraction decreases throughout the flame with increasing temperature. At the same time the soot agglomerate diameter decreases with increasing temperature as do the spherule diameters. This is in accordance with the reduction of the sooting tendency of premixed flames with increasing temperature reported by Glassman (1979).

On the other end of the spectrum, earlier work by Lahaye and Prado (1978) and Prado and Lahaye (1981) on the oxygen-free pyrolysis of methane and benzene indicates that in such a system the amount of soot formed increases with temperature. Spherule diameters decreased slightly with increasing temperature, and agglomerate dimensions were not measured. An increase with temperature in the sooting tendency of benzene during pyrolysis was also observed by Vaughn *et al.* (1981) during shock tube studies up to a temperature of about 2000°K.

Most diffusion flames may be considered to consist of a largely oxygen-free pyrolysis region surrounded by a flame front. It is the purpose of this study to determine the local soot concentrations and soot particle properties within such a flame.

II EXPERIMENTAL APPARATUS AND PROCEDURE

Burner

A Parker Wolfhard burner which supports two vertical flat flame sheets was chosen for this study in order to avoid the need for a deconvolution of the absorption signal necessary in flames of cylindrical geometry [see Jagoda *et al.* (1980) and Santoro *et al.* (1983)]. The burner, which is similar to the one used by Kent *et al.* (1981) and Haynes and Wagner (1980), consists of three parallel slots 51 mm in length. The outer slots, which carry the oxidizer, have a width of 16 mm each, while the inner fuel slot is 5 mm wide. For equal fuel and oxidizer burner exit velocities this results in a stable, somewhat underventilated flame. The burner is surrounded by a nitrogen-carrying jacket to exclude drafts and to prevent end-flamelets from forming across the width of the fuel slot. Further flame stabilization is assured by the use of screens near the tip of the flame. In order to permit steady operation over extended periods of time the burner housing is water cooled. The burner can be displaced in the vertical and horizontal directions to enable measurements to be carried out in different parts of the flame without disturbing the optical system.

Diagnostics

A simultaneous laser light scattering and absorption system similar to the one pioneered by D'Alessio *et al.* (1975) and described in detail by Jagoda *et al.* (1980) has been set up. The beam from a 4-Watt argon ion laser operating at 514.5 nm is focused into the test section in the flame using a 30 cm focal length lens and passes along the flat flame sheet onto a photomultiplier which measures the intensity of the transmitted light. A second photomultiplier is used to monitor the intensity of the beam scattered at 90° to the incident beam. A system of lenses and apertures limits the solid angle over which scattered light is collected and eliminates radiation from any part of the laser beam other than the 60 × 60 × 100 micron test volume under consideration. Direct radiation from the flame to the photomultiplier is reduced using a monochromator and a narrow band width interference filter. The remaining stray light is eliminated by placing a chopper in the incident beam and passing the output from the photomultiplier through a phase sensitive detector which amplifies only the signal in constant phase with the chopper, *i.e.*, radiation originating from the laser beam. The absorption and scattering signals are observed on an oscilloscope and registered on a chart recorder.

The Mie Theory in the Rayleigh approximation as detailed by Kerker (1969) is used to obtain the local soot volume fractions, F_v , the mean soot aggregate diameters, D , and number densities, N , of the soot agglomerates from the absorption and scattering measurements.

The scattering cross sections, C_{sca} , of the soot aggregates were determined from the measurement of the incident and scattered intensities of the laser beam, while the extinction coefficients, K_{ext} , were found from the incident and transmitted intensities (Beer-Lambert law). The mean scatterer diameters and their number densities were obtained from their scattering cross-sections and extinction coefficients, while the extinction coefficients by themselves yielded the soot volume fractions. The details of the mathematical relationships used have been derived from Kerker (1969) and are listed by D'Alessio *et al.* (1975), Haynes and Wagner (1980), Kent and Wagner (1982),

Santoro *et al.* (1983) and others. They will, therefore, not be repeated here. It is interesting to note that the determination of K_{ext} is less precise than that of C_{sea} since the absorption measurements integrate over the entire length of the flame and are, therefore, dependent on its two-dimensionality. Small deviations from perfect flame flatness and the possible existence of small end-flames reduce the accuracy in the determination of K_{ext} . Since N is proportional to the square of K_{ext} , their values may be expected to be less accurate than those of D which only varies as the inverse of the cube root of K_{ext} .

The determination of C_{sea} from the measurements of scattered intensity depends on a number of geometric parameters of the scattering system. Rather than measure these parameters, the system was calibrated with pure nitrogen and methane whose scattering cross-sections were calculated using expressions taken from Penney (1969) and Müller-Dethlefs (1979). The calculated scattering cross-sections of the calibration gases compared very well with these quoted by Rudder and Bach (1968) for the respective wavelengths. This technique has previously been used by D'Alessio *et al.* (1975) and Jagoda *et al.* (1980).

A monodisperse distribution of spherical soot particles was assumed. Therefore, when comparing the results presented in the next section with those obtained by Santoro *et al.* (1983), who assumed self-preserving or log normal distributions, the diameters determined here correspond to their $D_{6,3}$, while the number density must be multiplied by 2. Since in Santoro's treatment the soot volume fraction is given by $ND_{3,0}^3$ and the ratio $(D_{6,3}/D_{3,0})^3=2$, the soot volume fraction is unchanged.

The Mie theory of scattering in the Rayleigh approximation assumes spherical scatterers whose $D \ll \lambda$. This latter criterion is not strictly observed, but it can be shown that for particles of 100 nm diameter the error introduced is only of the order of 10 percent. Furthermore, the soot aggregates are not spherical and only "equivalent diameters" could, therefore, be established.

Both scattering and extinction measurements had to be averaged over excursions of the order of 5 percent in most parts of the flame. In areas of steep soot concentration gradients, these fluctuations due to small movements of the flame were somewhat bigger, but the results were, nevertheless, reproducible.

The optical measurements described above are a function of the properties of the agglomerates. The spherules which make up the agglomerates cannot be detected in this way. Soot was, therefore, extracted from various locations in the flame to determine the spherule diameter distributions using transmission electron microscopy. The effect of this procedure on the flame had previously been checked and found to be small (Jagoda *et al.*, 1980). Local degrees of agglomeration could, thus, be obtained by comparing the agglomerate dimension obtained from the optical measurements with the spherule diameters measured on the electron micrograph. When viewing the electron micrographs, extensive agglomeration can also be observed. This, however, is due mostly to agglomeration during sample collection and treatment, and is not representative of the degree of agglomeration in the flame. The diameters of the spherules, on the other hand, may be expected not to change because of the rapid quenching of the chemical reactions in the probe. It is, therefore, important to realize that the scattering and microscopy techniques are truly complementary.

The temperature distribution in the flame was measured using uncoated Pt, Pt-13% Rh thermocouples with a 125 micron diameter junction. Conductive losses were minimized by introducing the leads parallel to the flame sheet. Since relative temperatures rather than their absolute values are of interest here, the thermocouple results were not corrected for radiative losses.

Flame Temperature Variation in a Diffusion Flame

In this study the effect of temperature on the sooting process in a propane-air diffusion flame has been investigated. In the flame front of a diffusion flame the combustion proceeds, essentially, under stoichiometric conditions. For given fuel and oxidant compositions the adiabatic flame temperature is, therefore, essentially fixed. In order to be able to introduce a variation in adiabatic flame temperature for the diffusion flames, the inert nitrogen content of the oxidizer, which acts as a diluent, was varied. A decrease in nitrogen content, thus, corresponds to an increase in flame temperature, and vice versa. Results for flames of oxygen to nitrogen ratios, by mole, in the oxidizer flow of 0.27, 0.33 and 0.41 will be reported here. These flames will be referred to as "a", "b" and "c". Adiabatic flame temperatures T_{ad} , were calculated for these three cases taking into account the equilibrium concentration within the flame as computed using the NASA code developed by Gordon and McBride (1971).

III RESULTS AND DISCUSSION

Soot volume fractions, soot aggregate diameters and their number densities for flames of three adiabatic flame temperatures are reported here. They correspond to oxygen to nitrogen ratios of 0.27, 0.33 and 0.41 with calculated adiabatic flame temperatures of 2279, 2417 and 2540°K. The fuel was pure propane, and the cold gas velocity of fuel and oxidizer was maintained at 6 cm/sec for all cases.

Figure 1 shows the temperature distribution in the vertical plane normal to the burner slots for flame "a". It is observed that the flame front temperature remains constant with height in the part of the flame investigated. As one moves horizontally away from the flame front the temperature drops both in the direction towards the fuel and the oxidizer. In the pyrolysis zone, near the center, the temperature increases somewhat with height.

The temperatures in the flame fronts for the flames with higher oxygen to nitrogen ratios (*i.e.*, "b" and "c") were found to be above the melting point of platinum, causing the thermocouples to break. In order to obtain an indication of the relative temperature changes between the three flames, a shielded Pt, Pt-13% Rh thermocouple was used at selected positions in all three flames. This probe resulted in lower readings because of the heat loss due to the shield and no melting occurred. It was noted that the ratios between measured "shielded" temperatures in the flame front and calculated adiabatic flame temperatures were the same for all three flames within 1 percent. Flame temperatures for flames "b" and "c" were, therefore, extrapolated by multiplying the ratio between the unshielded measured temperature of flame "a" and its calculated adiabatic flame temperature by the calculated adiabatic flame temperatures for flames "b" and "c". Values for the flame front temperatures of 1973°K for flame "a", 2063°K for flame "b" and 2195°K for flame "c" were, thus, obtained. The shapes of the isotherm lines for the three flames are assumed to be similar.

The distributions of soot volume fraction versus distance from the burner center for different heights above the flame for the three flames are shown in Figure 2a, b and c. For all three flame temperatures the entire sooting region lies well within the fuel side of the flame and its soot content increases with height above the burner. The amount of soot produced at any given height above the burner increases with increasing flame temperature. Furthermore, comparison between Figures 2a, b and c shows that the increase in temperature leads to soot being formed earlier in the flame. Thus, the

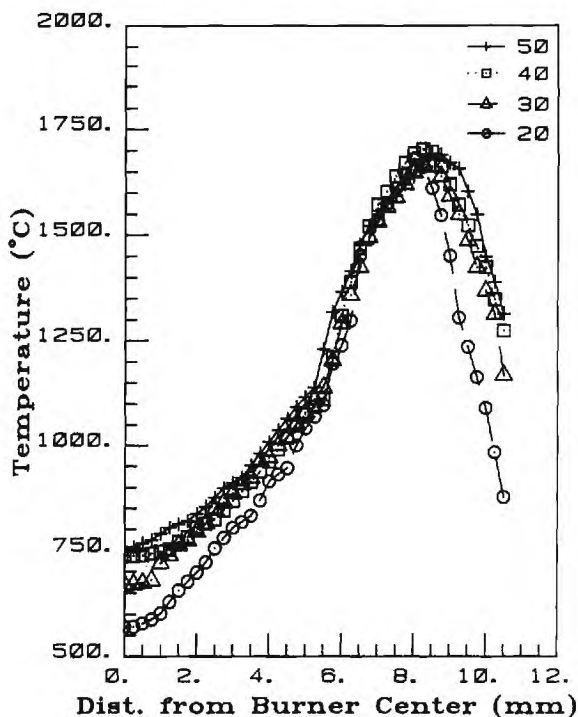


FIGURE 1 Temperatures versus distance from burner center at different heights above the burner for the flame with $T_{ad}=2279^{\circ}\text{K}$.

increase in temperature accelerates the production of soot precursors and pyrolysis products for soot growth in the lower region of the flame prior to soot formation. This occurs even though oxygen may be entrained into the pyrolysis zone due to quenching near the burner mouth which causes the anchor region of the flame to be more premixed in nature. In the upper part of the flame the increase in temperature results in an increase in pyrolysis rate, as postulated by Glassman *et al.* (1981). This leads to the observed increase in soot loadings and, therefore, to the increase in sooting tendency with temperature which they observed in diffusion flames.

In Figure 3 the mean soot aggregate diameters are plotted against distance from the burner center for different constant heights above the burner for the three different flames. For all cases the regions of maximum soot mass loading also correspond to those in which soot agglomerates of largest diameters are found. Clearly the mean soot aggregate diameters increase with increasing height in the flame for all temperatures investigated. Furthermore, the increase in temperature has the effect of increasing the soot agglomerate sizes found at given heights above the burner.

The aggregate number density distributions shown in Figure 4, on the other hand, follow a different trend. For all flames the maximum number of particles exists closest to the flame front. While more particles seem to be present near the flame front in the lower part of the flame than in the upper part, their number density decreases towards a common level in the region of maximum diameters and soot

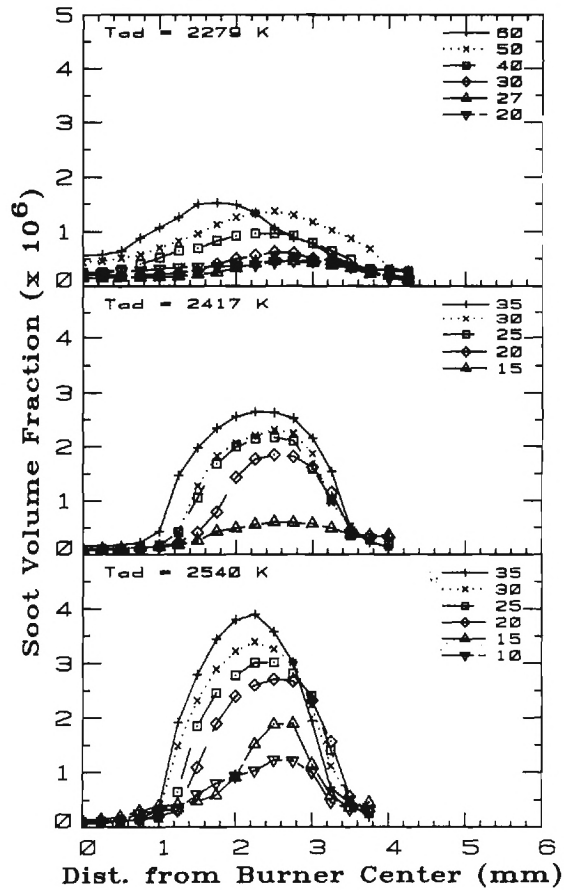


FIGURE 2 Soot volume fractions versus distance from burner center at different heights above the burner for three adiabatic flame temperatures.

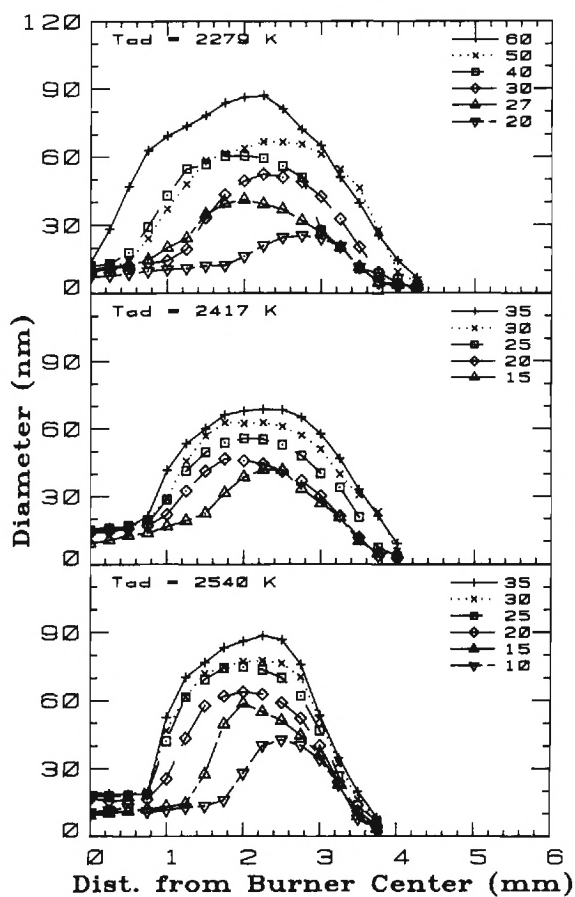


FIGURE 3 Soot agglomerate diameters versus distance from burner center at different heights above the burner for three adiabatic flame temperatures.

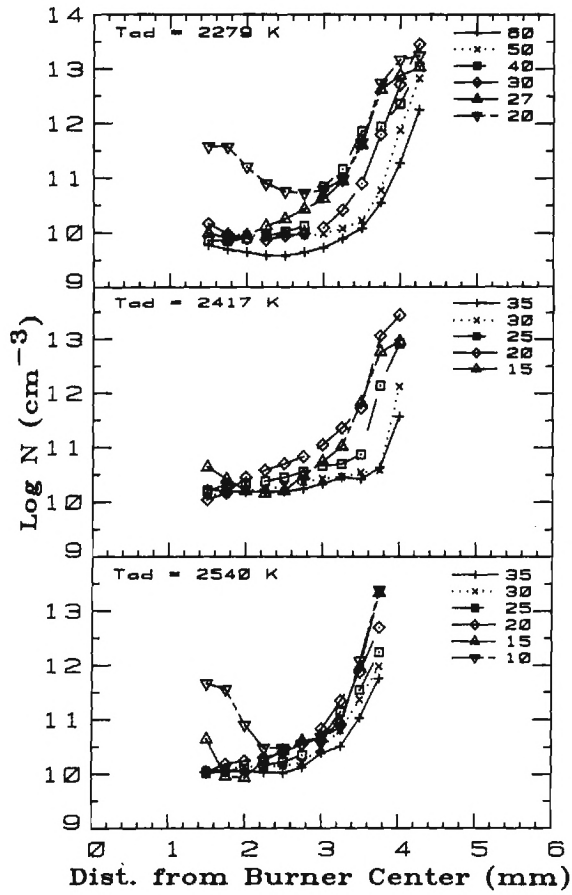


FIGURE 4 Soot agglomerate number densities versus distance from burner center at different heights above the burner for three adiabatic flame temperatures.

concentration. As mentioned in the previous section, the values of number densities are less reliable than those obtained for mean diameters and soot volume fraction because of their strong dependence on K_{ext} . Since the absorption near the burner center was relatively small and was influenced by the possible existence of end-flames and large polycyclic aromatic hydrocarbons in the fuel rich part of the flame, number densities are only plotted up to 1.5 mm from the burner center. For similar reasons the soot volume fractions and diameters near the burner center plotted in Figures 2 and 3 may be somewhat high. Careful inspection of Figure 3a indicates that there is a detectable decrease in the number density of soot particles with height above the burner suggesting an agglomeration in excess of the possible creation of new particles. Bearing in mind the reduced accuracy in the number density determination, it appears that there is little change in the number density with increasing flame temperature, except a somewhat smaller number of particles near the upper part of the flame front at higher temperatures.

The increase in soot volume fractions with temperature, therefore, appears to be due to an equal number of larger soot agglomerates being present in the hotter flames. Whether the increase in diameters of the mean soot agglomerates is due to an increase in the diameters of the fundamental spheroids which make up these agglomerates or to more extensive agglomeration could not be determined from the optical measurements. Soot samples were, therefore, extracted at heights above the burner at which the aggregate properties had been determined for the three flames. Unfortunately, the spatial resolution for sampling is not as good as that for the optical measurements, and only an average sample per height could be obtained. These samples were viewed under a transmission electron microscope and the diameter distributions of the soot spheroids were recorded. The mean spherule diameters are plotted versus height above the burner in Figure 5. The diameter of these elementary soot particles increases

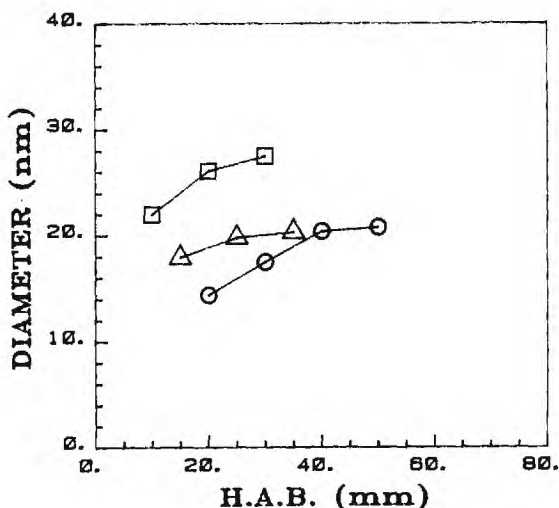


FIGURE 5 Mean spherule diameters versus height above burner for three adiabatic flame temperatures.

with height in the flame due to surface growth, for all three flame temperatures. This growth is particularly pronounced in the early part of the flame. Flames of higher temperature cause the formation of somewhat larger spherules. In particular, the soot spheroids found in the flame "c" are about 50 percent larger than those in the other two flames.

Since the agglomerates, unlike the spherules, are not spherical, their measured diameters correspond to "equivalent diameters". Their degree of agglomeration was estimated by comparing the mean volume of the spherules with that calculated using the equivalent diameter of the agglomerates as determined by the light scattering method. These degrees of agglomeration were determined using the largest mean agglomerate diameters observed at the different heights in each of the three flames. Table I indicates that the degree of agglomeration increases with distance in the flame for all three flames. The general trend in Table I suggests that, overall, the agglomeration process is accelerated by the increase in flame temperature from flame "a" to flame "b" but is slightly lower for the much larger soot spheroids present in flame "c" within the experimental accuracy.

TABLE I
Mean degree of agglomeration for flames "a", "b" and "c"

Ht. ab. Burner/adiab. fl. temp. (°K): (mm)	2279	2417	2540
10	—	—	7.3
15	—	12.9	—
20	5.6	—	14.7
25	—	22.3	—
30	27.1	—	22.6
35	—	38.6	—
40	26.1	—	—
50	33.4	—	—

The optical results described above are in good agreement with measurements carried out in flames using a different fuel by Kent *et al.* (1980) and by Haynes and Wagner (1980), as well as by Santoro *et al.* (1983) using a cylindrical burner. A leveling off of soot volume fraction in the upper part of the flame observed by Kent *et al.* (1980) was observed only in flame "a". Measurements in flame "b" and "c" were not carried out sufficiently close to their flame tips. Sampling to obtain spherule dimensions and, thus, degrees of agglomeration were not carried out by these workers. Nor did they investigate the effect of temperature on the individual soot parameters.

The overall steps in the formation of soot in diffusion flames as detailed by Haynes and Wagner (1980) appear to be valid for all flame temperatures investigated here. They are very briefly summarized for completeness and reconfirmed in light of the additional spheroid measurements reported here. For all flame temperatures the great majority of soot particles are created in the high temperature region near the flame front where the particle density is high but their diameters are small. This rate of nucleation seems to decrease somewhat with height above the burner especially for higher flame temperatures. As these particles move upward by convection as well as

away from the flame front towards the burner center by convection and thermophoresis, they grow by agglomeration as witnessed by the decrease in number density away from the flame front and their increase in degree of agglomeration with height above the burner. Agglomeration by itself, however, does not lead to an increase in soot volume fraction. This increase of soot loading must, therefore, be ascribed to surface growth as also indicated by the increase in spherule diameter in the downstream direction. The rate of surface growth has been shown to increase with flame temperature. This increase in the rate of soot formation due to surface reactions is likely to be due not only to an increase in gaseous species available for adsorption at the higher temperatures, but also to the larger surface areas presented by the larger spheroids. Some particles may also be formed as one moves towards the region of high soot concentration, but this generation rate must be small since the particle number decreases and the mean diameter increases in this direction indicating that aggregation predominates. This aggregation process is most pronounced in the vicinity of particle inception, *i.e.*, the number of particles decreases most sharply near the flame front. This may be due to the higher number densities leading to more frequent collisions in these regions, but it also indicates a greater tendency of the small, reactive "young" soot particles to stick together because of the presence of free radicals adsorbed on their surfaces. The process of aggregation, however, continues to some extent farther from the flame front as shown by the increase in degree of agglomeration with height above burner measured for all flames investigated. While an increase in temperature does not result in a noticeable change in aggregate number densities in the areas of appreciable soot loadings in the flame, more nuclei, which are not readily detectable, may be formed near the flame front of the hotter flames. An increased coagulation rate along with heavy surface growth in that region would then be responsible for the lack of change in aggregate number densities observed in the region where measurements can be made, while contributing to the larger spheroids and agglomerates found in the hotter flames. The smaller particles observed near the center of the flames may have been formed in the early part of the flame and have spent less time in the region of growth as suggested by Haynes and Wagner (1980).

In order to quantify the effect of the flame temperature on the global reaction rate of the soot formation reaction, the total soot volume fraction at different heights above the burner (*i.e.*, area under soot volume fraction plots) and the corresponding maximum aggregate diameters were plotted versus residence time. The residence time is defined as the time required for a pocket of gas to travel from the burner to a given height. This is not to suggest that all soot particles are formed near the burner mouth and grow as they move in a vertical direction through the flame. On the contrary, it has been shown that new particles are continuously being formed near the flame front at all heights. Since, however, the total soot loading at any given height in the flame is a result of the cumulative formation of soot up to that point, a fair comparison of the soot formation rates for different temperatures can only be obtained by comparing soot loadings in the flame for equal gas residence times. This takes into account any changes in vertical velocities due to the changes in temperature. Changes in thermophoretic velocity were neglected since these are only significant in the horizontal direction. A similar normalization was carried out for soot aggregates of maximum diameter at each height in the flame since the largest aggregates may be expected to, generally, result from soot spherules first formed in the early part of the flame.

Since no velocity measurements were carried out in this flame, the residence time in the flame had to be related to the height above the burner using theoretical considerations. Kent and Wagner (1980), who carried out velocity measurements in a

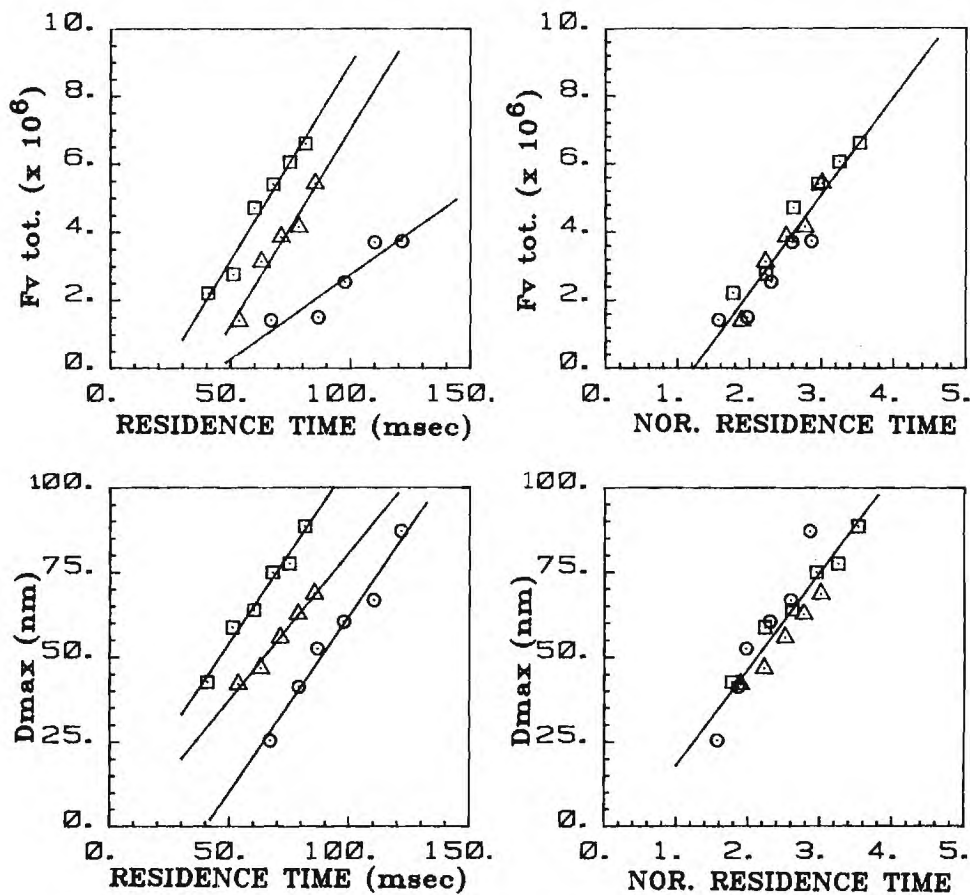


FIGURE 6 Total soot volume fractions at different heights above burner versus residence time (a), and normalized residence time (b); maximum soot agglomerate diameters at different heights above burner versus residence time (c), and normalized residence time (d).

similar diffusion flame, have established that buoyancy forces cause considerable acceleration of the vertical velocities in this type of flame. The relationship between the time required to reach a given vertical position and its height above the burner is, therefore, not linear.

A simple, one-dimensional model of two parallel streams of gases of differing densities based on the work by Powell and Browne (1956) was, therefore, developed. This model takes into account both the difference in density of fuel and oxidizer and the difference in temperature of the combustion products and the surrounding oxidizer flow. The details of this model are presented in the Appendix. Using the fuel and flame temperatures reported by Kent and Wagner (1980), their measured fuel velocities could be predicted with good accuracy, particularly by fitting the density ratio mentioned in the Appendix using the velocity measured at one point 90 mm above the

burner. This model was applied to the flames presented here and their vertical velocities were predicted from the temperature distribution measured. These vertical velocity distributions were used to convert the "height above the burner" into a time axis.

Figure 6a shows the variation of total soot volume fraction at given heights with residence time in the flame for all three flame temperatures. The increase in soot mass loading with temperature is clearly seen, while there seems to be a pronounced increase in soot formation rate (slope) in going from flame "a" to flames "b" and "c". The observed, less steep slope for flame "a" may, however, partly be caused by a leveling off in soot formation rate in the upper part of that flame.

A plot of maximum agglomerate diameter versus residence time (Figure 6c) shows that the rate of agglomerate growth (slope) is almost independent of temperature. The absolute values of the soot agglomerate diameters, however, are larger for higher flame temperatures. This increase with temperature is due, partially, to increased spherule diameters (Figure 5) and, partially, to increased agglomeration (Table I).

In order to normalize the data in Figures 6a and 6c and to obtain an "effective" growth residence time", which includes the effect of temperature on the sooting rate, the residence time for every height above the burner in each flame was divided by its residence time to the first measured appearance of soot. This was considered permissible, in spite of the difference in activation energy and, thus, the sensitivity to temperature of the nucleation and surface growth reactions, since both nucleation and considerable surface growth have taken place prior to the first experimental detection of soot at the base of the flame. Furthermore, nucleation continues at all heights above the burner, so that both nucleation and growth have taken place in each residence time interval over which soot measurements were carried out.

When total soot volume fractions are plotted against those normalized residence times, the points do, indeed, fall close to a single line as shown in Figure 6b. Similarly, Figure 6d shows an almost linear dependence of maximum diameters against normalized residence time.

IV CONCLUSIONS

The *in situ* soot parameters including soot loading, soot aggregate diameters and number densities, as well as spherule diameters have been determined for propane diffusion flames at three different flame temperatures. The general features of the distributions of these parameters are similar for all three cases and agree well with the observations made by other workers studying diffusing flames of different fuels at a single flame temperature. In addition soot spherule sizes and degrees of agglomeration were seen to increase with height above the burner for all flames studied.

As the flame temperature is increased, soot is beginning to be formed earlier in the flame. At the same time the soot loading at given heights above the burner increases. This more extensive sooting at higher temperature was found to be due to larger soot agglomerates which, in turn, are formed partially by an increase in the size of the spherules and partially by an increase in the degree of agglomeration. The agglomerate number densities are largely insensitive to the change in the flame temperature, although the number of incipient spheroids near the flame front, which are too small to measure, may have been affected. Even though buoyancy causes considerable acceleration of the flame gases in the vertical direction, the difference in temperatures

between the three flames is sufficiently small to affect the gas residence times in the flames by only a small amount (< 7 percent). All observations detailed above are, thus, still valid even when considering soot loading and particle diameters as a function of gas residence time in the flame rather than heights above the burner. The rates of growth of the maximum soot agglomerate diameters, as determined from the slopes of the curves of these diameters plotted against non-normalized residence time, appear largely insensitive to temperature. The absolute values of these maximum diameters, however, increase with flame temperature which accounts for the larger soot volume fractions observed in the hotter flames.

Lastly, it was shown that an "effective growth residence time" may be defined such that both total soot volume fraction and maximum soot diameters vary linearly with that normalized time for all flame temperatures. This is, of course, not to say that the rate of soot formation does not vary with temperature but rather that the effect of temperature may be included in the normalization. In conclusion, it is felt that the findings reported here help to shed new light on the global observation by Glassman (1979) and others, which have reported an increase of sooting tendency with temperature for diffusion flames.

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Appendix

CORRECTION FOR BUOYANCY

The model used to correct the velocity field in the flame for the effect of buoyancy is based on an analysis by Powell and Browne (1956) which deals with the investigation of the effect of the differing densities of cold fuel and oxidizer streams upon the fluid dynamic characteristics of diffusion flames. This model was expanded to take into account the effect of the differing temperatures of the combustion gases and the oxidizer stream upon their densities. The fuel at temperature T_f and oxidizer at temperature T_o are assumed to leave the burner in parallel streams with velocity u_i at height $y=0$. The cross-sectional area of the oxidizer and fuel streams at $y=0$ are A_{o_i} and A_{f_i} respectively. The streams are bounded on the outside by parallel walls, but the position of the interface between the two streams (which corresponds to the reaction zone) is free to vary with height such that the cross-sectional areas of the two streams also vary with height with $A_f + A_o = A = \text{constant}$. Frictional effects at the walls and the interface are neglected, and at each height the pressures in the two streams are equal. It is also assumed that T_o and T_f do not vary with height.

Applying Bernoulli's equation to each stream separately between stations o and y and using $P_f = P_o$ yields:

$$(u_o/u_i)^2 - (\rho_f/\rho_o)(u_f/u_i)^2 = \left[\frac{Y}{(u_i^2/2g)} \right] [(\rho_f/\rho_o) - 1] \quad (\text{A-1})$$

Conservation of mass for the two streams gives:

$$u_o/u_i = \frac{(u_f/u_i)}{(1+r)(u_f/u_i) - r} \quad (\text{A-2})$$

where the area ratio $r = A_f/A_o$. The density ratio ρ_f/ρ_o is given by

$$\rho_f/\rho_o = (m_f/m_o)(T_o/T_f) \quad (\text{A-3})$$

where m_f and m_o are the molecular weights of the fuel and oxidizer and the temperatures are absolute.

Equations (A-1) and (A-2) must be solved simultaneously in order to obtain the fuel and oxidizer velocities, u_f and u_o , as functions of height above the burner, y . The parameters that must be specified are the fuel/oxidizer area ratio, r , the initial velocity u_i , and the fuel and oxidizer temperatures, T_f and T_o . These latter values must be obtained from temperature measurements in the flame, and are needed to obtain the density ratio ρ_f/ρ_o . In solving these equations, it is convenient to use the dimensionless variables $U_f = u_f/u_i$, $U_o = u_o/u_i$ and $Y = y/(u_i^2/2g)$. A computer code was developed to solve equations (A-1) and (A-2) numerically by an iterative technique.

In order to evaluate the model, velocities were calculated for the ethylene/air flames investigated by Kent *et al.* (1981). For their burner $r=0.05$ and $u_i=7$ cm/sec. The temperatures T_o and T_f were estimated from the measured temperature profiles they presented for various heights. Thus T_f was taken to be 1300°K. The oxidizer temperature was more difficult to estimate so two cases were considered: (1) $T_o=300^\circ\text{K}$ (room temperature) and (2) $T_o=800^\circ\text{K}$ (mean between room temperature and T_f). The model predicts excessive vertical fuel velocities for $T_o=300^\circ\text{K}$ ($\rho_f/\rho_o=0.221$) and deficient fuel velocities for $T_o=800^\circ\text{K}$ ($\rho_f/\rho_o=0.615$). A curve fit was also obtained by matching the experimental data at 90 mm by choosing $\rho_f/\rho_o=0.368$. This gives excellent agreement with the experimental data down to 30 mm. The small deviations of the experimental data from the theoretical curve for heights below 30 mm are most likely caused by vertical temperature gradients in the flame. This model was used to calculate the vertical velocity distribution in the flame which, in turn, was used to convert "heights above the burner" to time elapsed from the instant a pocket of gas leaves the burner mouth. These calculations showed that while the gas velocity in the flame is strongly affected by buoyancy (6 cm/sec at the burner mouth to 85 cm/sec at 5 cm above the burner for flame "a") the difference in residence time to reach a given height for the 3 flames is small (*e.g.*, 83.6 msec in flame "a", 78.5 msec in flame "b" and 74.8 msec in flame "c" to reach a height of 30 mm above the burner). The increase of soot content and soot aggregate diameter with increasing temperature is, thus, valid even when considering the data as a function of "time elapsed" rather than "height above burner".

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