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FINAL TECHNICAL REPORT

CHEMISTRY OF COMBUSTION OF FUEL-
WATER MIXTURES

Submitted by:

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ARC No. 47-5748   October 1979

ATLANTIC RESEARCH CORPORATION
ALEXANDRIA, VIRGINIA · 22314

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ABSTRACT

An experimental flame study is reported of the nonphysical processes that lead to soot suppression when water is added to fuel. In practical systems water, emulsified into liquid fuels, reduces soot physically by producing improved atomization and also chemically by altering some soot formation process. To investigate the chemical aspects alone, a gaseous laminar diffusion flame was used, which type of system eliminated the physical part of the process. A flame structure study was performed in which complete chemical species, temperature and soot profiles were measured through flames with and without water added. A flame with added nitrogen was also mapped for comparison purposes.

The study to date is somewhat incomplete; however, the following results can be reported. It appears that soot reduction by water addition is a result of a lowering of temperature throughout the dark zone of a diffusion flame with accompanying reduction in soot formation rates. Water is more effective in this respect than equivalent amounts of nitrogen, leading to the conclusion that water has a chemical inhibiting effect on some exothermic reactions early in the flame, in addition to its thermal effect.

An important finding was that there were high concentrations of oxygen present in the fuel zone of the diffusion flame. A concentric tube burner was used with the inner tube carrying fuel and the outer tube air. It is shown that air can diffuse across the rim of the burner at rates comparable to that of the fuel flow. This finding may have important implications for combustion modeling.

A soot sampling method was also developed in the course of the program which is ideal for measurements in certain types of flames and which represents a significant advance over other methods in rapidity and reproducibility.

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INTRODUCTION

The primary purpose of this study was to determine the nature of the nonphysical processes which cause water, when added to fuel, to suppress soot formation. By way of introduction to this report, a short discussion of soot formation processes is presented.

The burning of most fuels is accompanied by the production of soot. Under proper conditions fuel is converted to carbon particles in certain flames. These particles radiate, producing the yellow color found in the so-called "luminous zone" of a flame. In some cases, the carbon will be consumed by oxidation, while in others it will be released as free soot. Thus, even though some flames will be highly radiative they will not necessarily result in the formation of soot deposits. The radiation can at times be useful -- such as in certain furnaces or in the light produced by a candle flame -- although it is usually undesirable in military applications. Soot is almost never desirable in a combustion process.

In the future, when we will be forced more and more to rely on synthetic fuels, the problem of carbon and soot formation can only worsen (1). This is due to the fact that the synthetic fuels contain a higher percentage of aromatics than do conventional petroleum fuels. A good measure of the sooting tendency of fuels is their hydrogen/carbon ratio. The lower the ratio, the greater the sooting tendency. This ratio is low for aromatics and thus for fuels with high aromatic content. Conventional petroleum fuels, containing typically 10 to 15% aromatics, have a H/C atom ratio of about 2. Synthetic fuels derived from coal can have more than 50% aromatic content, and have H/C ratios on the order of 1.25 unless extensive processing is performed. The H/C ratio of shale oil is intermediate to the petroleum and coal-derived liquids.

The mechanism or mechanisms of soot formation are not generally agreed upon although they have been the subject of hundreds of articles. A review by Palmer and Cullis (2), a chapter in the text by Gaydon and Wolfhard (3) and articles by Porter (4) and Howard (5) contain much of the information necessary for probing the subject. The problem can be separated into a physical and a chemical part, the chemical dealing with the formation of soot

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precursors from fuel and the initiation of the nucleation process, while the physical part concerns the limitation of growth of particles to a certain size.

The nature of soot formed in flames is independent of the type of fuel used or the conditions under which the fuel is burned. Physically, soot consists of spherical particles with dimensions of the order of several hundred Angstroms. These spheres are usually attached to each other so as to form what looks like a string of beads, with larger agglomerates that form what look like clusters of grapes. There are conflicting reports in the literature on the structure of these spheres (see references 2 and 23 for a thorough discussion of the subject). One study reports that micrographs show that the particles are constructed of graphitic layer planes in an onion-like or spherically concentric structure. The layer spacing is close to but greater than graphite, with distortions and dislocations. Other studies report that these spheres of several hundred Angstroms consist of smaller crystallites which in turn have dimensions of the order of a few tens of Angstroms. The structure of the smaller crystallites is close to that of graphite, although the planes are randomly stacked and have spacing approximately one-tenth Angstrom greater than the 3.35 $\overset{\circ}{A}$ spacing in pure graphite.

A model has been proposed by Howard (5) which explains the growth of crystallites and their agglomeration into larger spheres. The model is based on an assumption of ionic nuclei being either the actual precursor species or the result of a neutral precursor acquiring a charge. Howard develops an expression which relates the charge on a particle to its size. The electrostatic repulsion between crystallites prevents agglomeration until the particles are large enough to sufficiently separate the charges to allow collisions. The size necessary for agglomeration under normal flame conditions was predicted by Howard to be of the order of 20 to 30 Angstroms, in agreement with experimental values. The agglomerates then grow, adding charges, until collisions are no longer possible due to the lack of sufficient kinetic energy to overcome electrostatic repulsion. Chains then begin to form due to the fact that the most probable contact points for charged spheres and

charged bodies are at the ends of the bodies. Further reports (6,7), however, indicate that the above approach is too simplified, in that most particles in a flame are not charged, and the crystallite size necessary for agglomeration may not be accurate.
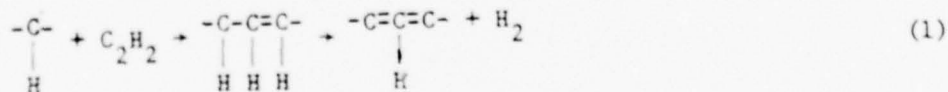
Chemically, soot formation occurs differently in diffusion and premixed flames. In diffusion flames, soot production is dependent on the C/H ratio of the fuel, and decreases in the order:

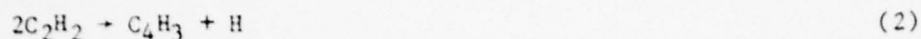Naphthelenes > Benzenes > Acetylenes > Diolefins > Monolefines
> Paraffins (8).

In premixed flames, the C/O ratio is also important (2) and the above order does not hold.

Many species have been hypothesized as soot precursors including: C, C_2, C_3, CH, C_2H, C_2H_2, polyacetylenes, C_6H_5, and positive ions ($C_mH_n^+$) (3,5). Two general and virtually exclusive mechanisms have been suggested (2): Either direct polymerization of the fuel followed by dehydrogenation, or degradation of fuel molecules to simpler species followed by reaction with fuel molecules or fragments and accompanied by dehydrogenation.

Many specific mechanisms have been suggested (2) having various degrees of credibility. One scheme which has gained some acceptance (4,9) involves the decomposition of all species to acetylene prior to soot formation. Porter (4) states that acetylene is converted directly to carbon and hydrogen without involving either C_2 or any higher hydrocarbon. He considers the key nucleation step to be:
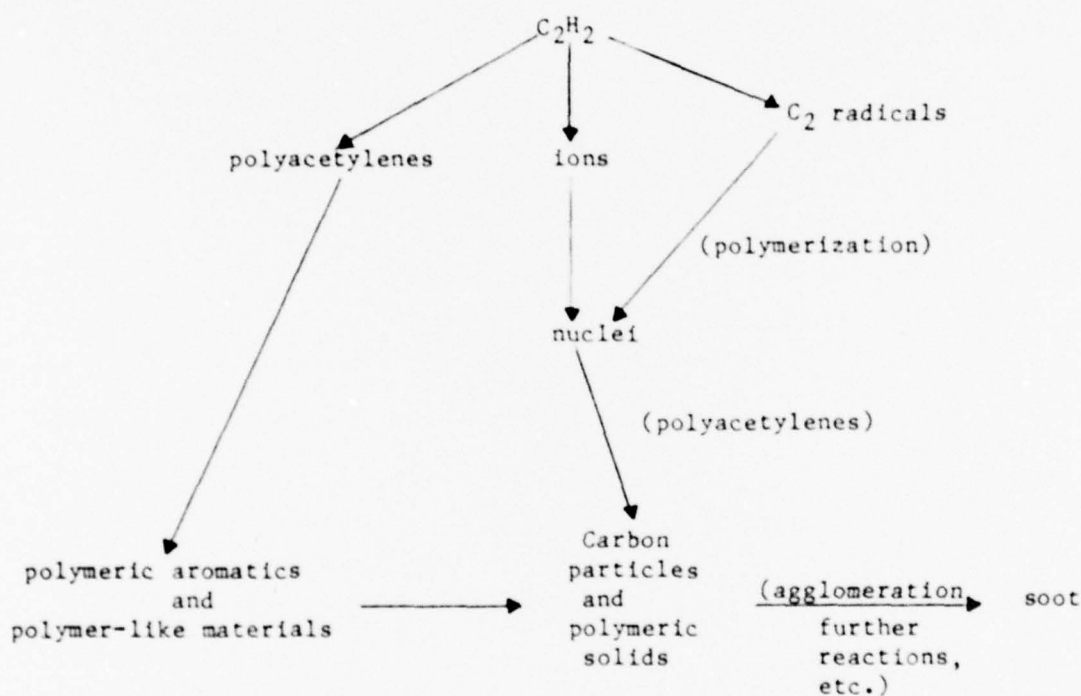
$$-\overset{|}{\underset{H}{C}}- \ + \ C_2H_2 \ \rightarrow \ -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{H}{C}}=\overset{|}{\underset{H}{C}}- \ \rightarrow \ -C=\overset{|}{\underset{H}{C}}=C- \ + \ H_2 \tag{1}$$

Gay, et al. (10), however, found that acetylene decomposed thermally to yield polyacetylenes, i.e., higher hydrocarbons:

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$$2C_2H_2 \rightarrow C_4H_3 + H \tag{2}$$

$$C_4H_3 + M \rightarrow C_4H_2 + H + M \tag{3}$$

$$C_4H_2 + C_2H_2 \rightarrow C_6H_3 + H \tag{4}$$

$$C_6H_3 + M \rightarrow C_6H_2 + H + M \tag{5}$$
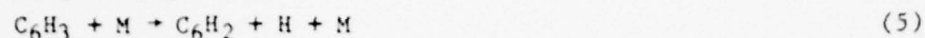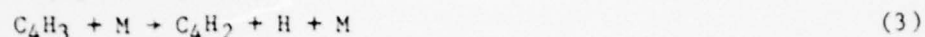
etc.

In a review article dealing with acetylene combustion, Williams and Smith (11) presented a scheme for the formation of soot from acetylene involving many routes:

Aromatics, though highly sooting, are probably not soot precursors. Palmer and Cullis (2) state that benzene pyrolyzes to produce diacetylene which is a soot precursor. In general, any highly unsaturated aliphatic may serve as a soot precursor.

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The addition of water to fuels can greatly reduce carbon formation. As an example, one can consider the case of adding water to fuel oil as an emulsion. The amount of excess air necessary to eliminate smoke can be greatly reduced by the addition of water to the fuel. The gain realized from the reduction of air more than compensates for the energy loss from the water additon. A specific study (12) can be cited to make this quantitative. The addition of 20% by weight of water to fuel oil in a commercial boiler (equivalent to about one percent of the total fuel and air) was found to allow a reduction in the excess air from 28 to 12% by weight, without increasing the level of smoke (soot) emission. At constant stoichiometric ratio, the quantity of smoke dropped by a factor of 3 to 4. This resulted in an increase in efficiency of about 2% as measured by temperature change across a heat exchanger.

The suppression of soot formation by water is due to more than one process. Dryer (13) and Jacques, et al. (14) have studied the purely physical effect of water/oil emulsions on soot formation. Droplets of the emulsion (generally 20% by weight water) were observed to burn not smoothly but with violent rupture of the droplets. The so-called "microexplosions" or "secondary atomization" is due to the boiling of the water within the oil droplet.

These microexplosions apparently account for only a part of the suppression of soot formation. Researchers who have studied the process believe that an important effect of water on soot formation is chemical -- due to one or more chemical processes. Some of these processes will now be mentioned.

In the case of liquid fuel, the cooling produced by the added water might lessen the likelihood of liquid-phase pyrolysis and thus reduce the production of carbon (14). This carbon, however, does not have the crystalline structure of soot, being more coke-like.

Secondly, water could reduce the temperature in the fuel-rich zone of diffusion flames which would lower the rate of soot formation.

Thirdly, water could act directly with the carbon particles after they form, according to the so-called "producer gas" reaction:

$$C + H_2O \rightarrow CO + H_2 \qquad (6)$$
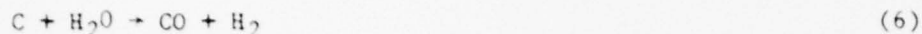
Next, soot, after formed, could react with OH radicals which might be produced from the available water (13,14) by the reaction:

$$H + H_2O \rightarrow H_2 + OH \qquad (7)$$
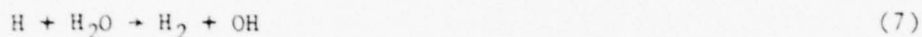
This is kinetically unlikely in diffusion flames, where in the fuel-rich region, water would be competing unsuccessfully for H atoms with the fuel itself, according to the reaction

$$H + RH \rightarrow R + H_2 \qquad (8)$$
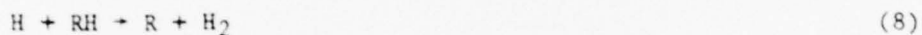
The relatve rates of reactions (7) and (8) can be estimated. The rate constant for reaction (7) is approximately $10^{14.4} \exp[-21,000/RT]$, and for reaction (8) approximately $10^{14} \exp[-7000/RT]$ in units of cc/mole sec (22). The constant for reaction (8) is an estimate based on reference (22) data and will of course vary for different fuels (RH). Assuming roughly equal molar concentrations of fuel and water vapor, the ratio of the rate of reaction (8) to reaction (7) at, say, $1200°K$ is well over 100, and even at $1800°K$ is still approximately 20. Hence, this chemical explanation for the effect of H_2O is ruled out for diffusion-type combustion.

Finally, there is the possibility that water could react directly with one or more soot precursors such as C, C_2, C_3, CH, C_2H, C_2H_2 and C_6H_5. Plausible reactions can be hypothesized for all these species with water, which would then tend to reduce the level of soot production.

In the present study, it was desired to study the chemical effects of water independently from the physical, to determine which chemical effects are responsible for the reduction of soot. Ethylene was chosen as the fuel for this study as, in diffusion flames, it is intermediate in its degree of sooting.

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EXPERIMENTAL

A. Description of Apparatus

A burner consisting of two concentric tubes was constructed for the diffusion flame studies. The inner tube, which measured 19 mm inside diameter, was used to carry the ethylene as well as the water or nitrogen additives where appropriate. The outer tube, measuring 135 mm in diameter carried the air. Both tubes were packed alternately with a series of gauze layers and fine mesh screens. These served to provide laminar flow with flat profiles. The flame was further stabilized by another fine mesh screen set on top of the inner tube, and by a short 70 mm diameter chimney on top of the outer tube. The fuel tube could be moved vertically relative to the air tube. Greatest flame stability was achieved when the fuel tube was positioned within a few millimeters either above or below the top of the chimney. Since sampling, especially low in the flame, was facilitated when the burner tube was above the chimney, this particular orientation was used for the bulk of the flame probings. Stability was further increased by isolating the burner in a fume hood from which the ventillation system had been disconnected. The result was a flame which was visually steady with the exception of occasional slight flickering at the tip.

Since it was desired that a measurable amount of soot be obtained during an experiment while at the same time not being overwhelmed by the amount of soot, ethylene was used as the fuel. This gave a moderate amount of soot, intermediate to fuels such as low sooting methane and high sooting acetylene.

C.P. grade ethylene and, when necessary, prepurified nitrogen were metered into the burner flow tube through calibrated critical orifices. The same method was used to meter compressed air into the outer air tube.

In the experiments in which water was used as an additive, the ethylene was bubbled through a flask containing heated water. The tubing leading to the burner as well as the inner burner tube were heated to above 100°C to prevent condensation of water vapor on the walls. During this phase of the

experiment, the gauze layers and screens within the fuel tube became essential to reduce the turbulence caused by temperature gradients in the tube. In addition, a needle valve was installed downstream of the bubbler. By reducing the aperture of the valve, pressures in the system could be equalized, preventing the flame from "bumping."

Rather than rely on theoretical vapor pressure data and saturation to determine water vapor concentration in the fuel, the water vapor was condensed and quantitatively collected in cold flow tests to determine concentration as a function of temperature of the bubbler.

The lines leading to the burner were sufficiently long to allow complete mixing of the ethylene and nitrogen or water vapor when appropriate, before entering the burner tube.

Profiles through the diffusion flames with and without additives in two dimensions were obtained for soot, chemical species and temperature. The various sampling devices were connected to a micromanipulator which allowed probe positioning to less than 0.5 mm precision in both vertical and horizontal directions.

Temperature profiles were obtained with a 2 mil bare wire Pt/Pt 10% Rh thermocouple connected to a potentiometer. Soot buildup on the thermocouple bead was minimal as the temperature at any one flame position could be measured in a matter of seconds. The soot could then be either physically knocked off, or burned off by maneuvering the bead into an oxidizing part of the flame. Corrections due to radiative cooling of the thermocouple were applied. At the maximum flame temperature (about 1950°K) the correction amounted to about 100°K. Future plans call for coating of the thermocouple bead.

The method used to sample the soot is one that was developed in this laboratory as a part of the program. A paper describing this method has been accepted for publication by Combustion and Flame (15) and is included as an appendix to this report. Briefly, a narrow sliver of glass is quickly inserted into the flame at a predetermined height for a measured amount of time, and quickly withdrawn. Soot deposits on the glass correspond to the

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concentration through the flame. This was then scanned with a densitometer and the resulting optical density data were converted to soot flux via a pre-calibrated conversion scheme.

Species profiles were obtained using a quartz probe in conjunction with an EAI Quadropole Mass Spectrometer. The probe was constructed so as to perturb the flame as little as possible. Using dimensions suggested by Fristrom and Westenberg (16), the probe was constructed of 3 mm o.d. quartz tubing tapered at a 20° angle to a 100 micron orifice. The probe was connected via Teflon line to a tee -- one branch leading to a vacuum pump, the other branch leading through a needle valve to the mass spectrometer. Consistency of total sample pressure was maintained at 6×10^{-6} torr ion gauge pressure by the needle valve. Clogging of the probe was not a problem, since an individual mass spectrum could be obtained in a matter of seconds, and it took longer than two minutes for the probe tip to become clogged to the point that needle valve monitoring could no longer keep the pressure constant.

B. Experiments Performed

The probing of the three diffusion flames (neat C_2H_4, H_2O added, N_2 added) with regard to soot, chemical species and temperature produced a large amount of data. Sampling was performed at 0.5, 1.5, 2.2, 2.9, 3.3 and 3.6 cm above the burner. For chemical species and temperature, samples at every 1 mm from flame center to flame edge, and every 2 mm from there outward to 12 mm from the center were taken. Entire soot profiles were obtained at each height, and densitometer readings were taken every 0.5 mm.

RESULTS AND DISCUSSION

A. General Observations

It was found that a steady flame was obtained when ethylene was flowing at a mass flow rate of 2.72×10^{-3} g/sec, corresponding to a linear flow velocity of 0.83 cm/sec at room temperature; and air was flowing at 4.26×10^{-1} g/sec corresponding to a linear flow velocity of 10.2 cm/sec. These air

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and fuel rates were always used regardless of whether or not additives were present. Attempts to slow the air flow so as to make the two velocities more equal resulted in too much flickering to allow accurate measurements.

Using fuel and air at the above rates, resulted in a flame 3.6 cm in height, with the dark zone extending to 2.2 cm above the burner. All soot was consumed within the luminous zone, with none existing at the flame tip. Addition of either water or nitrogen to the fuel did not change the flame height, as the increased flow velocity was compensated by the dilution of the fuel. When water was added to the flame in various amounts, it was found that the luminous zone began to disappear (turn blue) at about 0.5 mole fraction of water, and the luminous region became entirely blue with about two thirds mole fraction of added water. When probed, no soot was present in the blue region. Using nitrogen insted of water, the N_2 mole fraction had to be greater than 0.8 to arrive at the totally blue flame.

The actual experiments on the flame with water added were conducted on a mixture which was 30% water vapor by volume (21% by weight). This value was chosen to roughly conform to the quantity of water used in fuel oil in operational systems. There was no visible change in the color of the flame at this water concentration, but the effect on soot concentration was definite, and will be discussed in a later section.

The amount of nitrogen used was the amount needed to set the temperature at 0.5 cm above the burner in the center of the flame identical to that of the water flame. This resulted in a 47.4% N_2 mixture. Again, no visible change in flame color could be seen in this mixture.

B. Temperature Measurements

Temperature profiles of the neat, H_2O-added and N_2-added flames are shown in Figures 1, 2 and 3, respectively. In addition, contour drawings of the isotherms for the three flames, derived from interpolations of the temperature profiles are depicted in Figure 4. An isotherm drawn between the 1200 and 1300°K isotherms in each of the three flames would roughly parallel the shape and position of the dark zones.
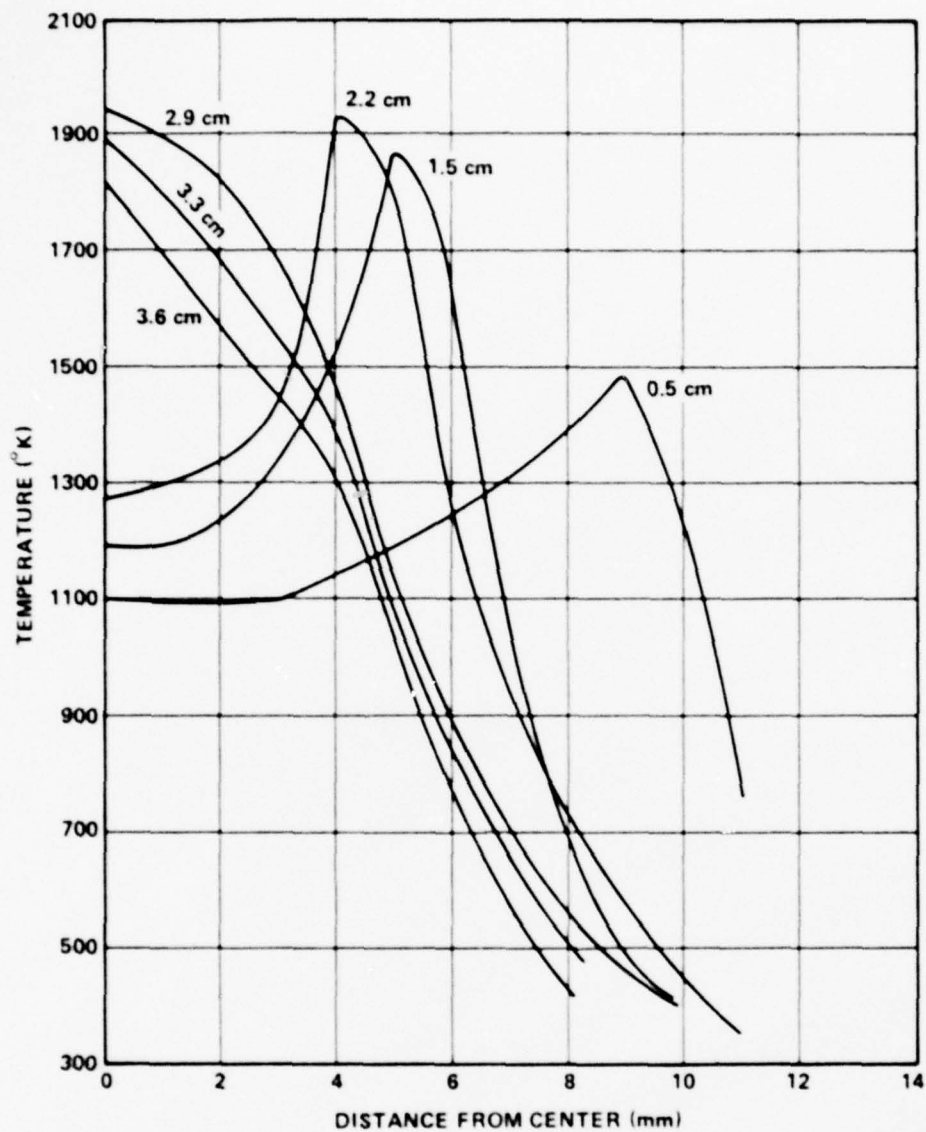
10

Figure 1. Temperature Profiles for C_2H_4/Air Diffusion Flame at Various Heights above the Burner.
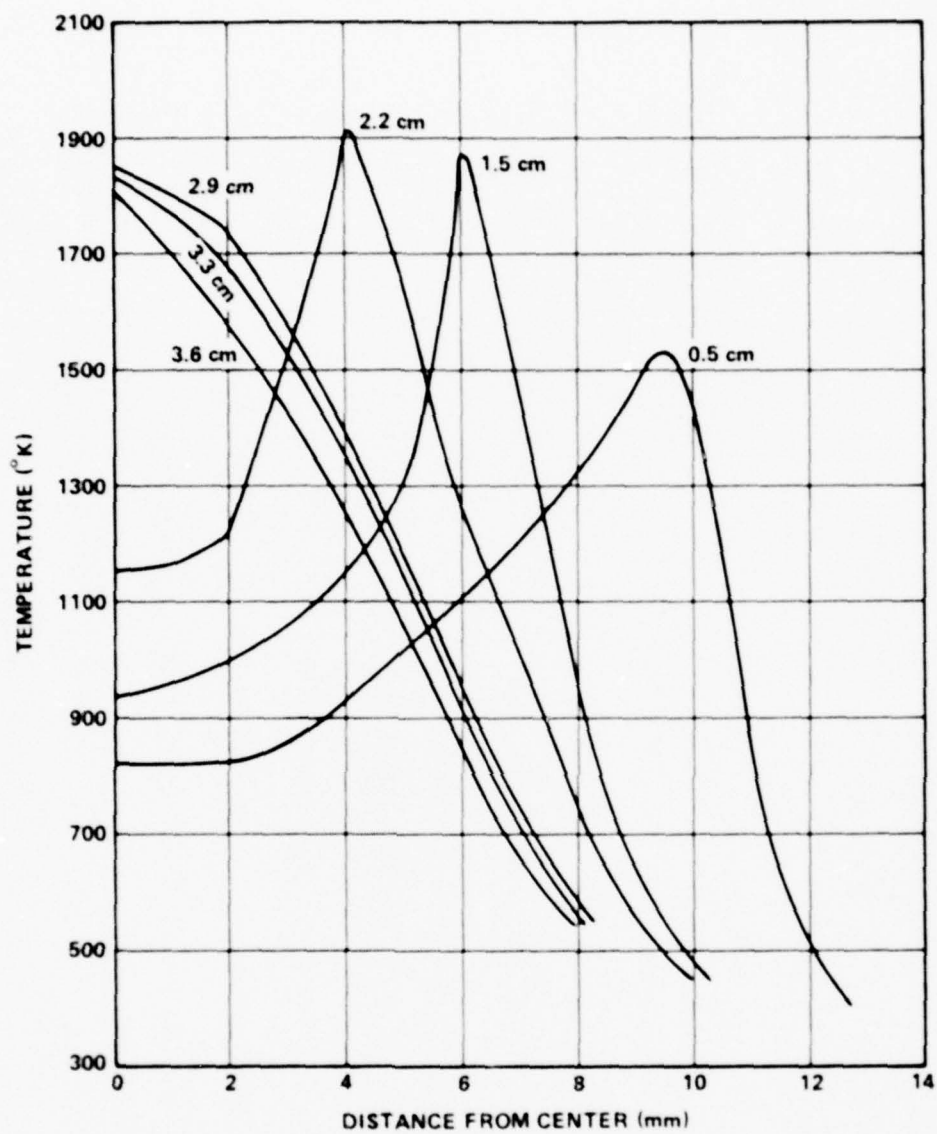
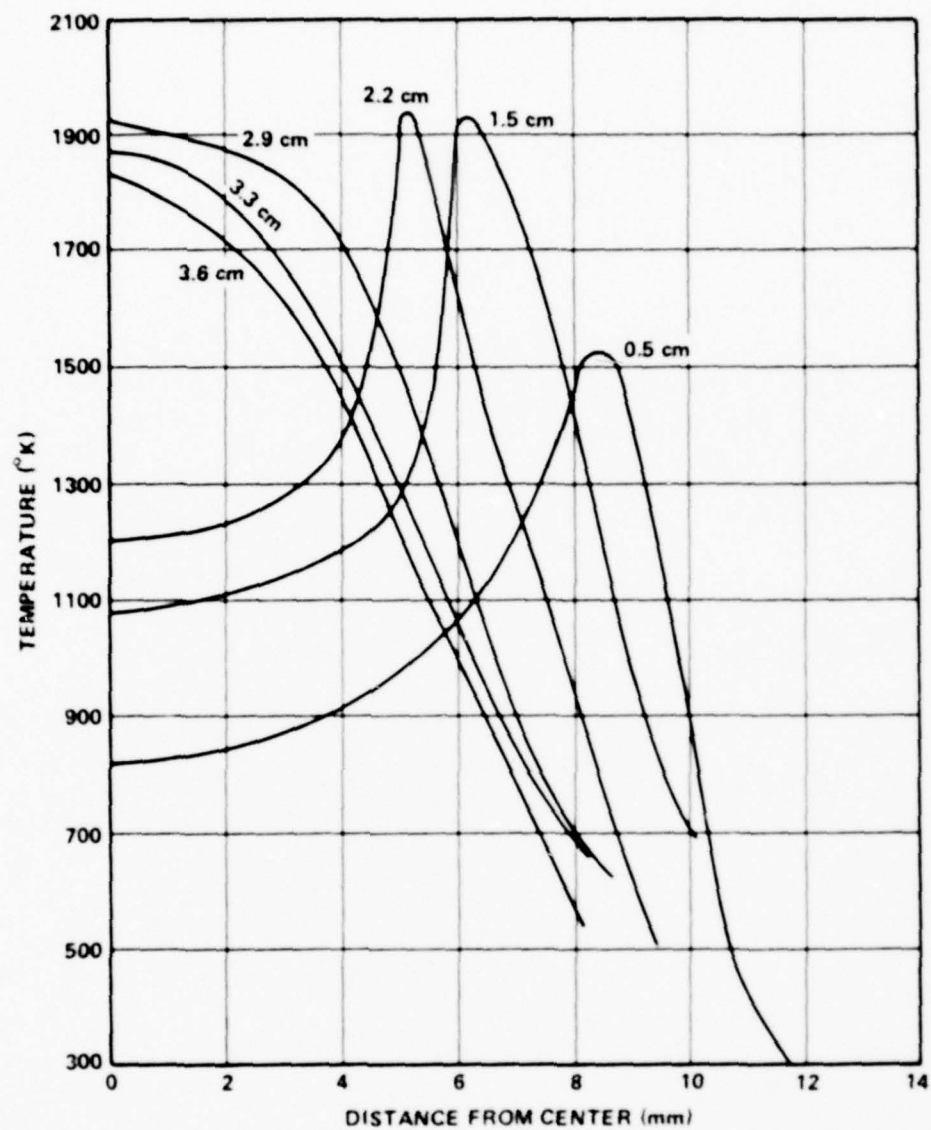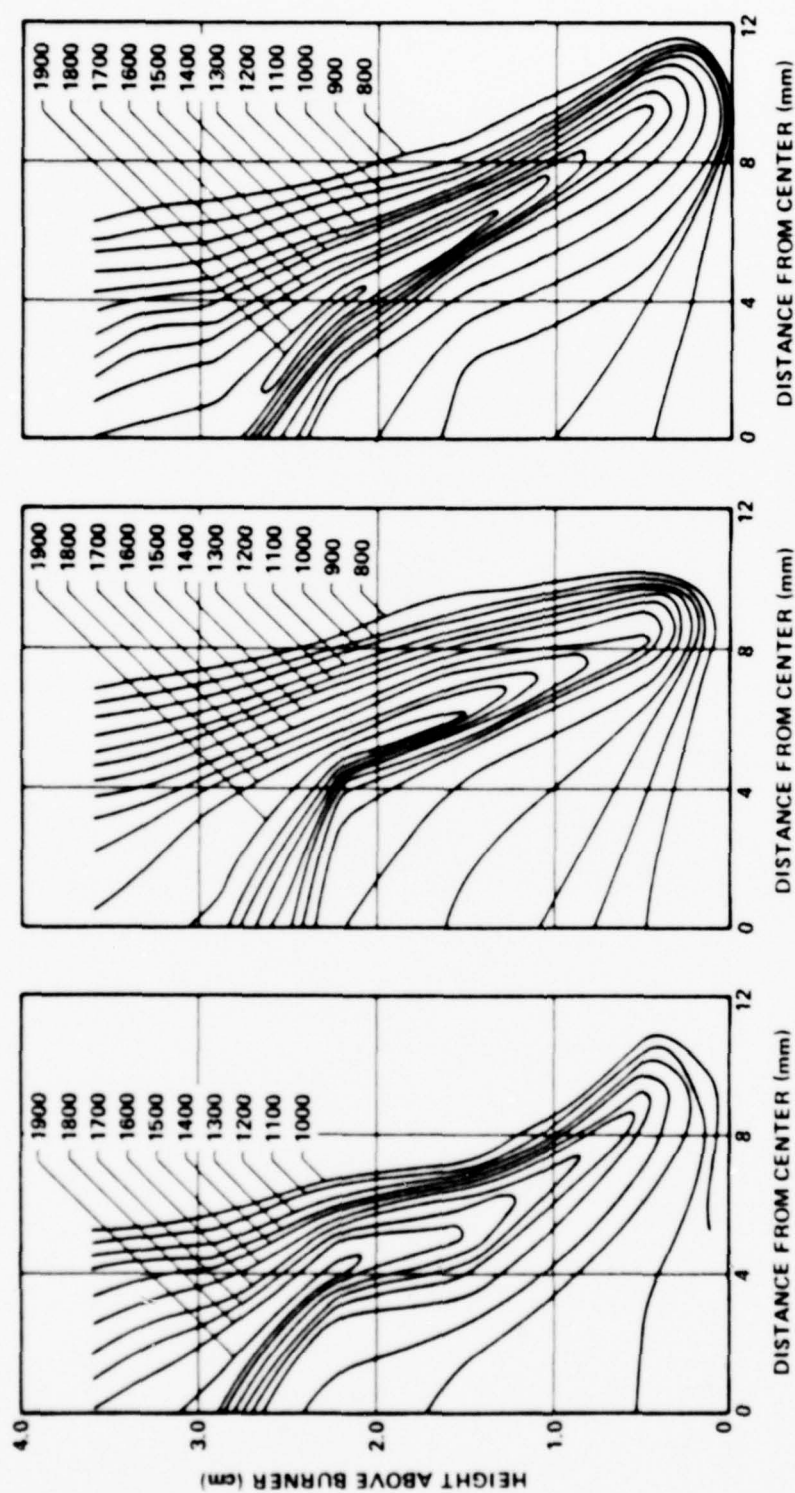Figure 2. Temperature Profiles for C_2H_4-H_2O/Air Diffusion Flame at Various Heights above the Burner.

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Figure 3. Temperature Profiles for $C_2H_4\cdot N_2$/Air Diffusion Flame at Various Heights above the Burner.

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(a) C_2H_4/Air Flame.

(b) C_2H_4-N_2/Air Flame.

(c) C_2H_4-H_2O/Air Flame.

Figure 4. Contour Diagrams Depicting Isotherms for Various Diffusion Flames ($°K$).

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The main thermal effect of added water or nitrogen was a lowering of temperature within the dark zone. Outside this region, smaller temperature decreases were found. The maximum temperature of each flame occurs a few mm above the dark zone, being about 1925°K for the neat and nitrogen-added flames, and slightly (about 50°) lower for the water added flame. Whether the measured difference between N_2 and H_2O flames is real or not at these elevated temperature is not known.

Taking the center vertical axis of the flame as an example, the temperature profiles of the three flames can be compared (Figure 5). Since the three flames are of the same size, comparisons can be made at any particular flame height. It can be seen that the addition of water or nitrogen has a definite effect on the temperature of the dark zone. The addition of 30.2 mole percent of water lowers the temperature nearly 300°K at 0.5 cm above the burner. The equivalent lowering at that position is achieved by adding 47.4 percent of nitrogen. Higher in the dark zone it can be seen that water is more effective in lowering temperature. For instance, at 1.5 cm, the difference between the temperatures of the neat and water-added flames is about 240°C, while the nitrogen-added flame is only about 100°C cooler than the neat flame.

It is necessary then to look at the pure "heat-sink" effect of both water and nitrogen. The heat needed to raise the temperature of water, nitrogen and ethylene from 298 to 1000°K is 25.9, 21.3 and 50.6 kJ/mol (6.2, 5.1 and 12.1 kcal/mol), respectively (17). The nitrogen-added flame has 47% N_2, thus a relative heat-sink effect for nitrogen is $0.47 \times 21.3 = 10.0$ kJ/mol (2.4 kcal/mol). The water-added flame has 30% water, and this heat-sink effect is $0.3 \times 25.9 = 7.8$ kJ/mol (1.9 kcal/mol). Thus, on a purely thermal basis, nitrogen should reduce the temperature 2.4/1.9 or 1.26 times more than water does. Looking at the data at 1.5 cm above the burner, the nitrogen flame is about 100° cooler than the neat flame. The water flame should then be only about 80° cooler than the neat flame. Instead the temperature is approximately 240° lower. Therefore the cooling effect of water is not attributed only to the presence of this additive as an inert diluent, but also must be exhibiting a chemical effect. The most likely explanation is that water is inhibiting exothermic chemical reaction in the dark zone.
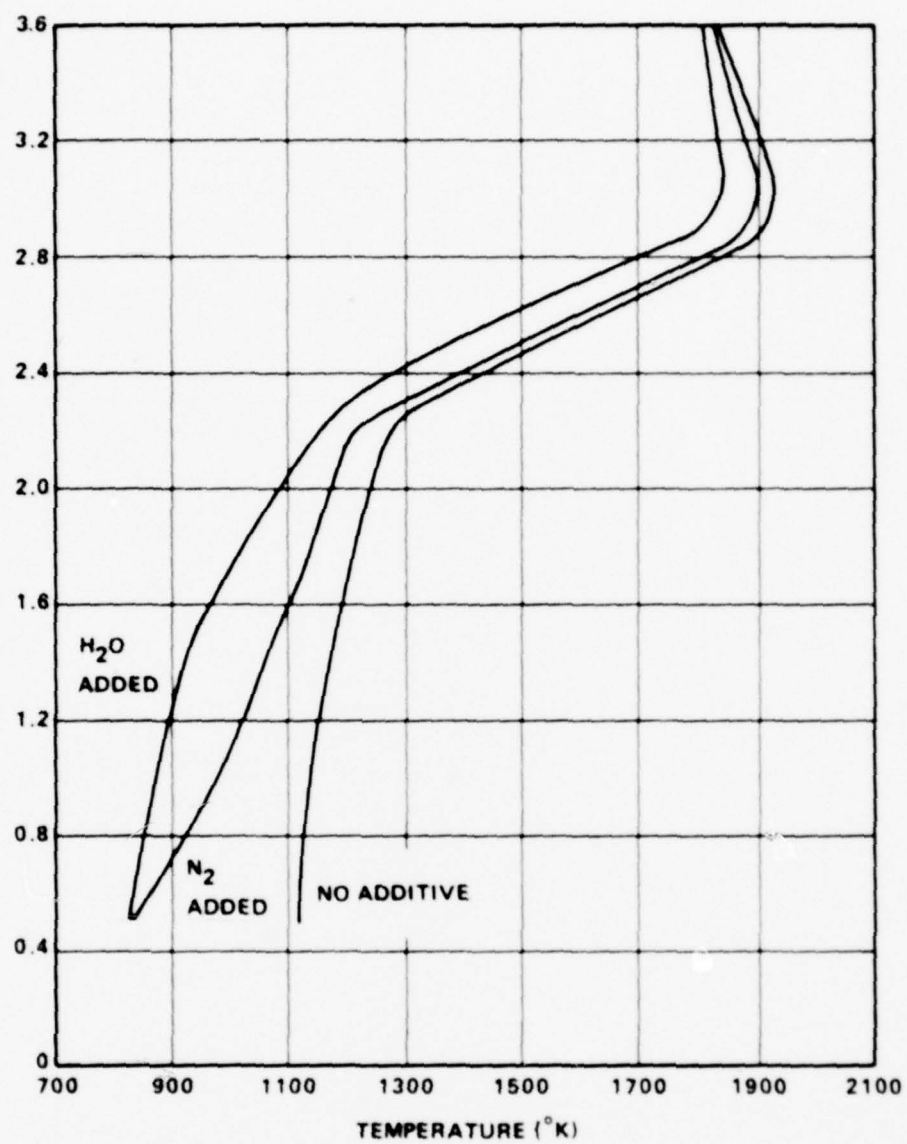
15

Figure 5. Temperature Profiles for the Various Diffusion Flames
Along the Central Vertical Axis.

C.   Measurements of Chemical Species

Mass spectrometric scans of the three flames provided profiles of six major species: O_2, H_2, H_2O, C_2H_4, C_2H_2 and CO_2. CO is also a reaction product, but it was not possible to measure its concentration due to the masking of its base peak (m/e = 28) by both N_2 and C_2H_4. Vertical concentration profiles for the six aforementioned species along the central axis of the neat, water-added and nitrogen-added flames are shown in Figures 6, 7 and 8. A major feature of these profiles is the presence of oxygen in large concentration in the fuel zone of the diffusion flame. Numerous tests were made to assure that the presence of oxygen was not an artifact of the experimental system. The presence of oxygen was reproducible and followed a definite pattern. In each of the three vertical profiles (Figures 6-8), the concentration of ethylene is seen to decrease rapidly, diminishing by nearly an order of magnitude between 0.5 and 1.5 cm above the burner. Yet, a corresponding increase in product concentration (H_2, C_2H_2, CO_2 and presumably CO) is not realized. In addition, in Figure 7, which represents the profile for the water-added flame, the decrease in the concentration of water nearly parallels that of ethylene. Therefore the decrease in ethylene concentration is attributed heavily to dilution as well as to chemical reaction and decomposition. The same figures show increases in oxygen concentration at the same flame positions, and oxygen as it enters the fuel zone is accompanied by the nitrogen in the air.

It is desirable to account for the presence of air within the fuel zone, comprising as it does a second source of oxygen for the diffusion flame as can be seen from Figures 9 - 11. One possible explanation is that air diffuses in just above the burner rim. The height of this peripheral zone would correspond to the quenching distance of the flame and thus should be of the order of 1 to 2 mm. Visual inspection of the flame also shows a dark zone of about this dimension. A rough estimate of the magnitude of a diffusion flux across this zone can then be obtained from the relationship
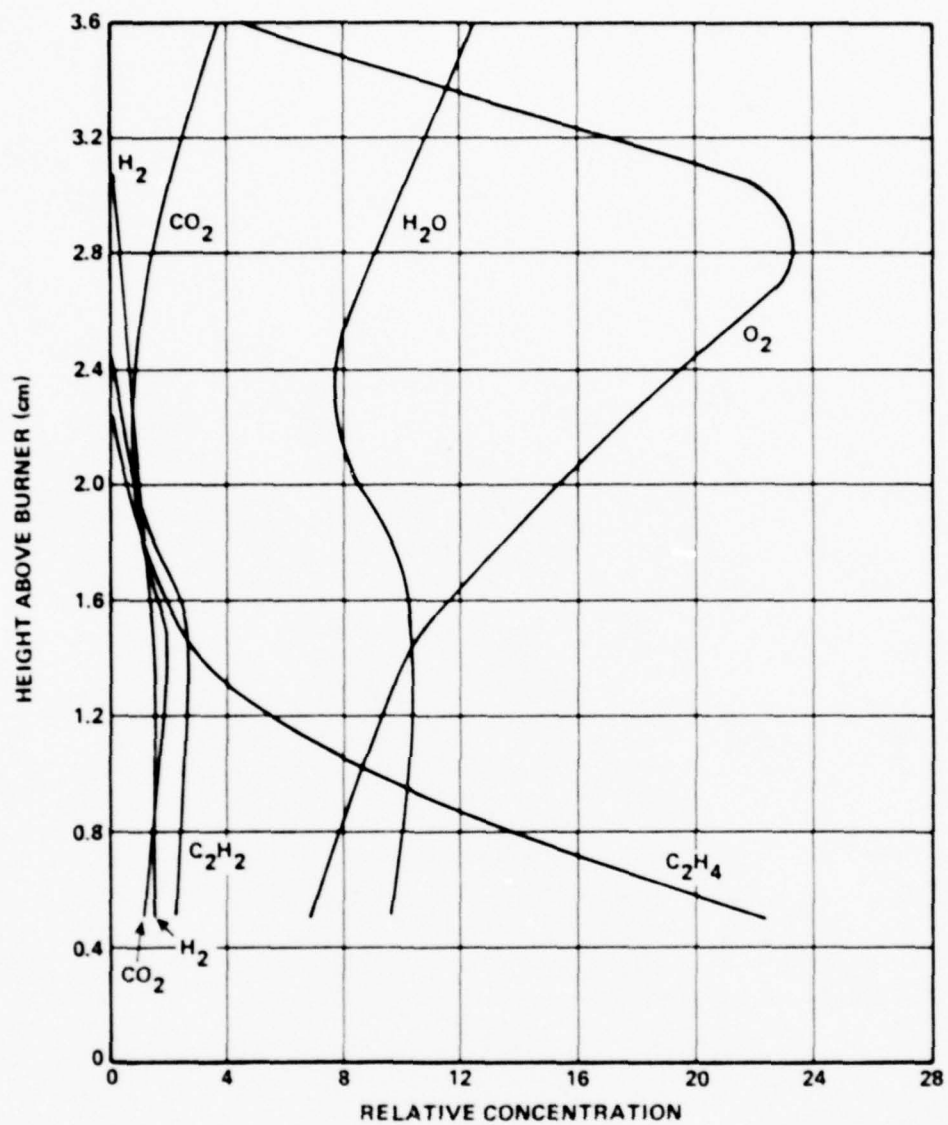
$$F = Dc/\Delta x$$

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Figure 6. Profiles of Various Species Along the Central Vertical Axis of a C_2H_4/Air Diffusion Flame.
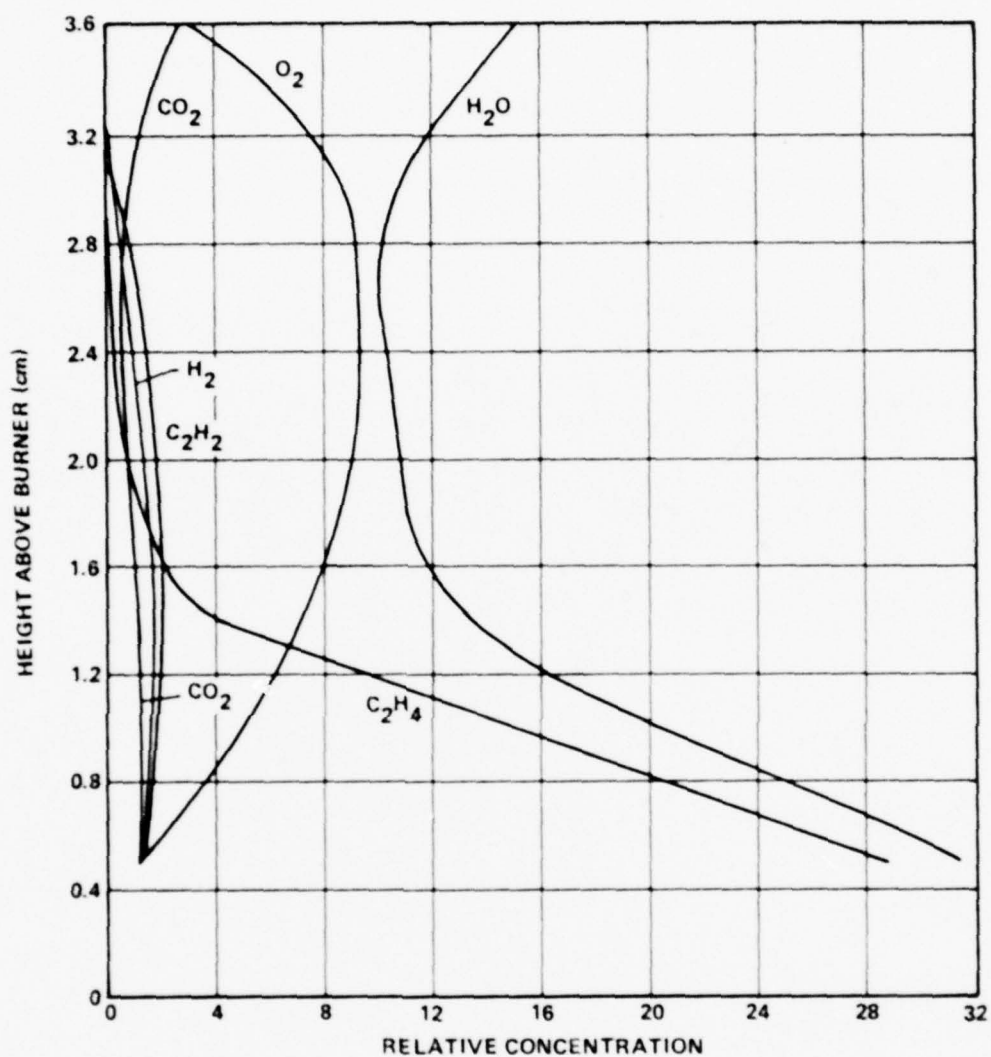
18

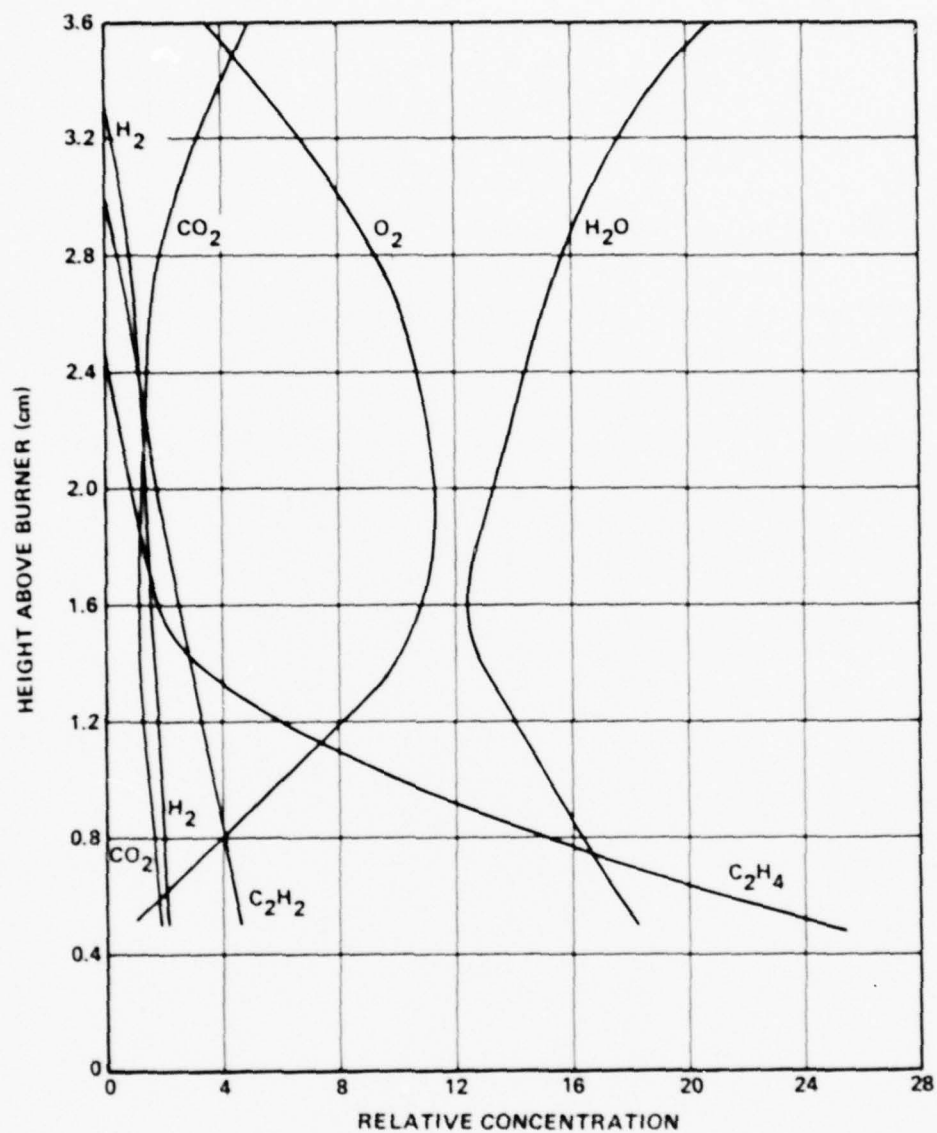Figure 7. Profiles of Various Species along the Central Vertical Axis of a C_2H_4-H_2O/Air Diffusion Flame.

Figure 8. Profiles of Various Species Along the Central Vertical Axis of a $C_2H_4 \cdot N_2$/Air Diffusion Flame.
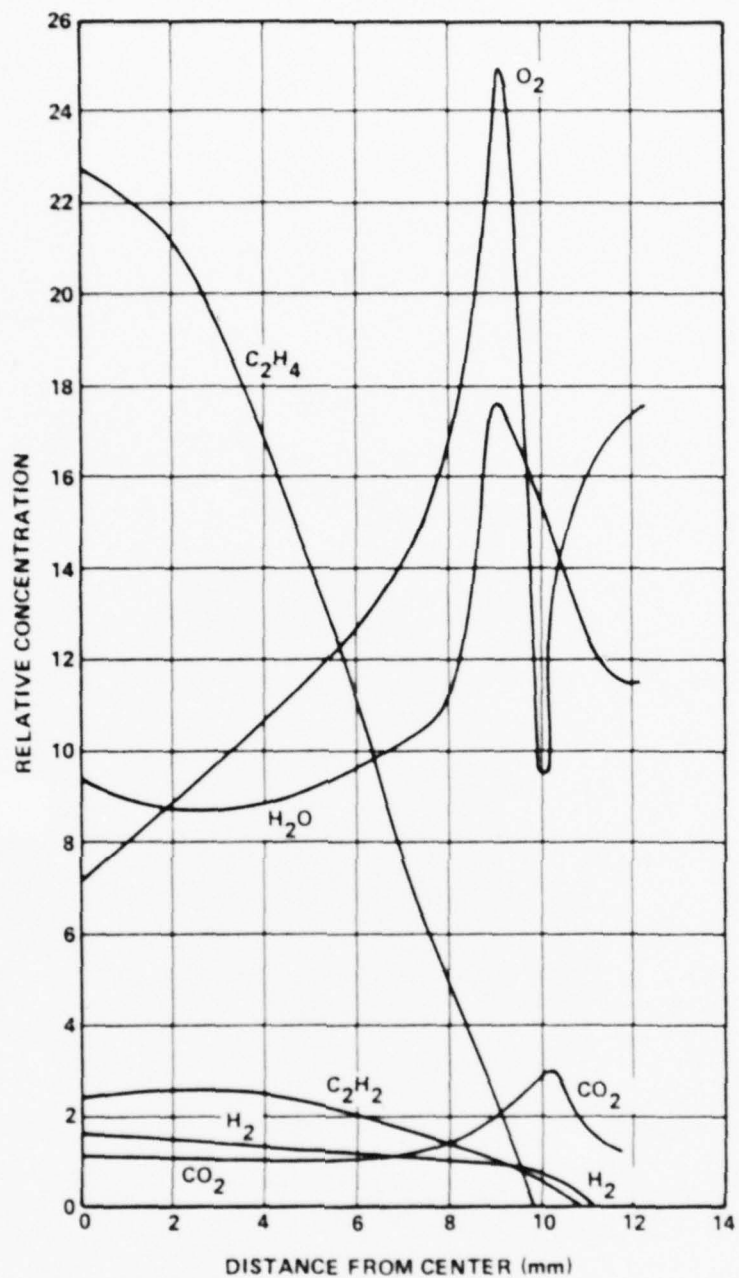
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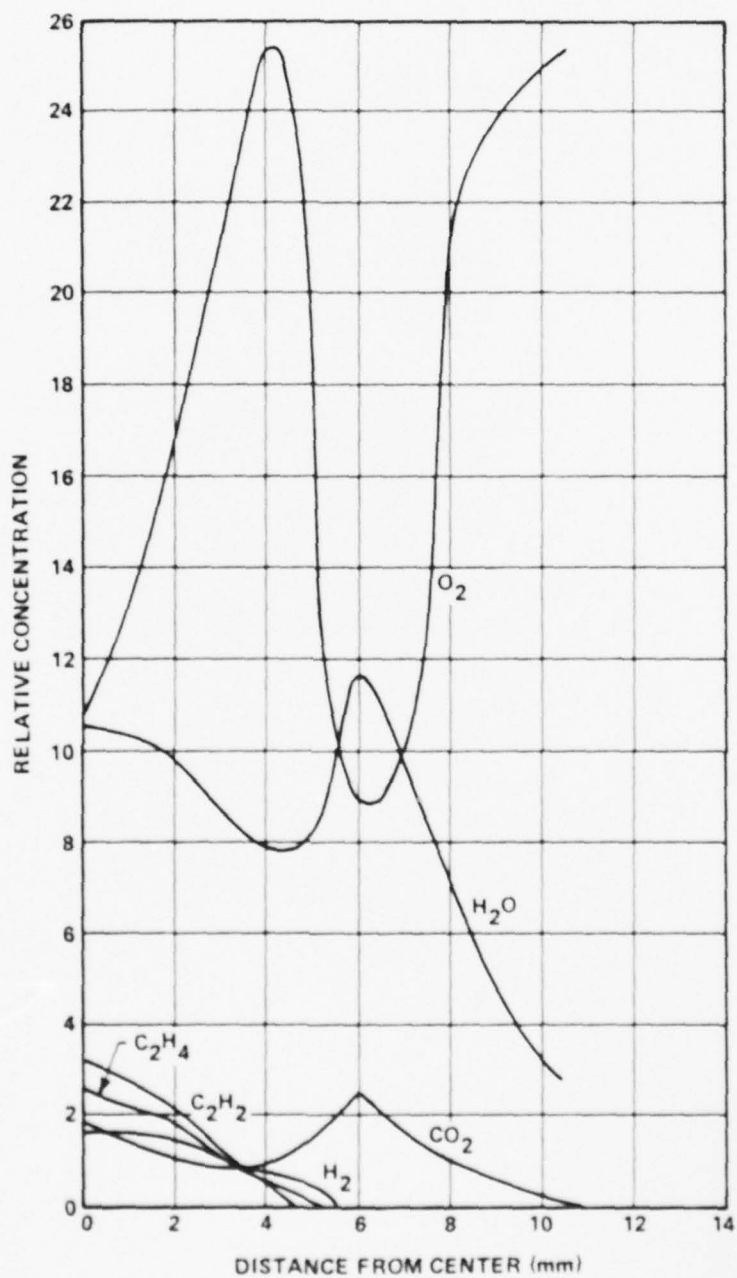Figure 9. Horizontal Profiles of Various Species 0.5 cm above the Burner in a C_2H_4/Air Diffusion Flame.

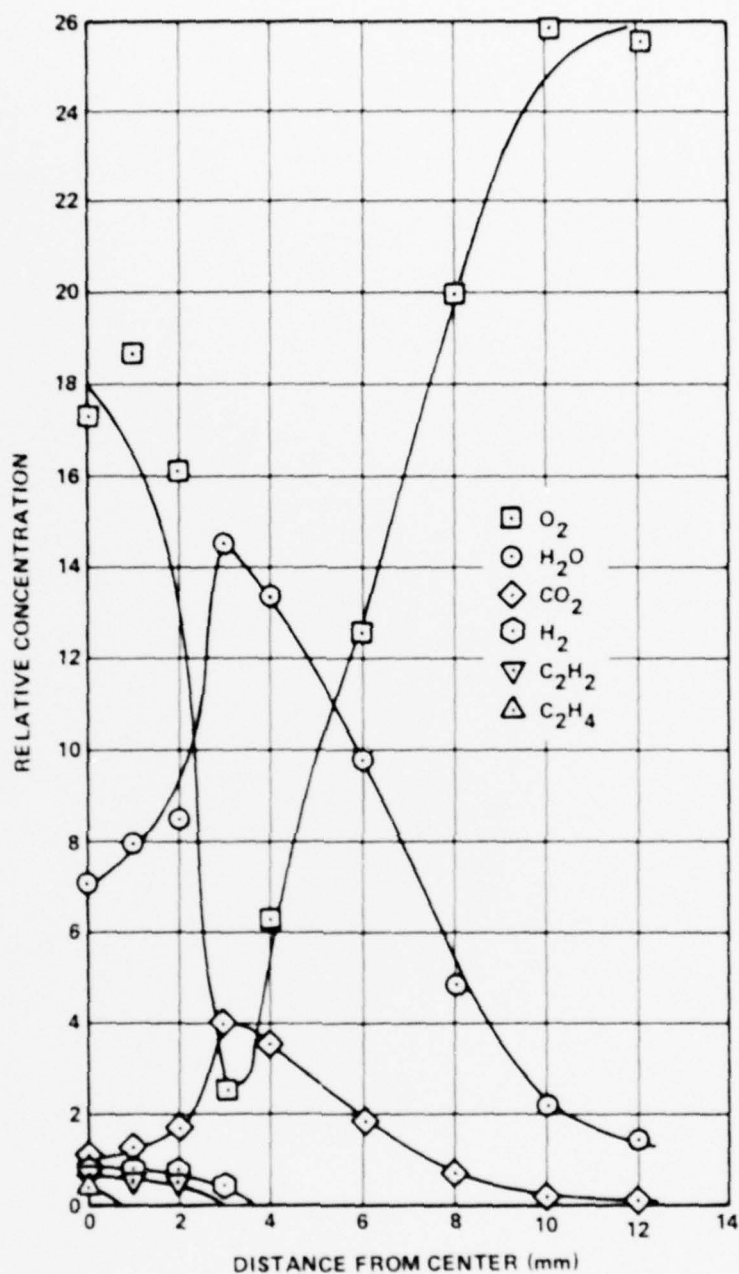Figure 10. Horizontal Profiles of Various Species 1.5 cm above the Burner in a C_2H_4/Air Diffusion Flame.

Figure 11. Horizontal Profiles of Various Species 2.2 cm above the Burner in a C_2H_4/Air Diffusion Flame. (Data points are shown on this plot to illustrate precision of measurements. The points are omitted on other figures.)

Where D is the diffusion coefficient and $c/\Delta x$ represents the concentration gradient. The following values for these quantities are assumed: A typical handbook value for D is $0.2 \text{ cm}^2/\text{sec}$ at ambient conditions. If a mean temperature over which diffusion occurs is taken as about 1000°K, then D will increase to an average of around $1.5 \text{ cm}^2/\text{sec}$. The concentration, c, can be taken as the ambient density of air adjusted to 1000°K, or about $0.4 \times 10^{-3} \text{g}/\text{cm}^3$. Considering the oxygen profile of Figure 9, it appears that a value for Δx of approximately 0.1 cm should be used, which distance corresponds to the maximum of the O_2 concentration and to the "inside" of the diffusion flame. On this basis the diffusion flux of air across the rim of the burner is computed to be of the order of $6 \times 10^{-3} \text{g}/\text{cm}^2\text{sec}$. The mass diffusion flow through the entire peripheral quenching zone would be of the order of $5 \times 10^{-3} \text{g}/\text{sec}$. This quantity refers to air and the oxygen flow would be one fifth of it.

The flow rate of ethylene fuel in all the experiments was given earlier as $2.72 \times 10^{-3} \text{g}/\text{sec}$. The comparability of this value with the estimated diffusion flow of $5 \times 10^{-3} \text{g}/\text{sec}$ lends considerable support to the assumption that air enters the fuel zone through the quenched region above the burner rim. It is probably not worthwhile to carry this analysis further unless a more rigorous approach is used.

Other workers have obtained results in probing experiments of diffusion flames of various types that also show the presence of oxygen in the fuel zone. References 18 and 19 are some example studies. Burke and Schumann (20) also show profiles wherein oxygen is present with the fuel in an underventilated flame. Excepting for reference 19, attention has not been called to the oxygen presence. It is not inconceivable that this presence could have an important effect on diffusion combustion, especially that of droplets. Analytical modeling of such processes should consider whether this is an important point.

In this same connection it can be noted that Fenimore and Jones (21), using a burner design very similar to that of the present study, report no oxygen in the fuel zone. This finding is completely consistent with and

reinforces the assumption of air diffusion across the burner rim in our system when one considers the manner in which Fenimore and Jones performed their experiments. In their tests there was just enough oxygen admixed with fuel to provide a flat premixed and very sooty flame on top of the inner fuel tube. The main diffusion flame anchored on top of the premixed flame. Therefore, any air diffusing in at the burner rim would be consumed in the premixed flame and no molecular oxygen would appear in the diffusion flame.

Other features of the present flames can be seen in the species profiles presented in Figures 9 - 13, as well as in the center-line profiles of Figures 6 - 8. Three flames were completely mapped in two dimensions, resulting in a large volume of data. Only a few of the profiles were chosen for presentation in order to provide a general picture of flame compositions without overwhelming the reader. Figures 9, 10, 11 show the profiles for the neat flame in the region of greatest interest at 0.5, 1.5 and 2.2 cm above the burner. Figures 12 and 13 then give the profiles at 1.5 cm above the burner for the water- and N_2-added flames for comparison with Figure 10. Data points are shown only in Figure 11 to provide an idea of the precision of the method.

It is apparent that ethylene converts to acetylene and hydrogen, presumably by the elementary molecular reaction:

$$C_2H_4 \rightarrow C_2H_2 + H_2 \tag{9}$$
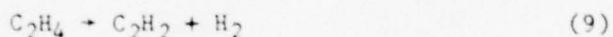
which is 174.5 kJ/mol (41.7 kcal/mol) endothermic. It is not known whether direct ethylene oxidation also occurs or whether decomposition is more rapid and the products C_2H_2 and H_2 are the species oxidized. The system is too complicated to derive reaction rates for these competing oxidation and decomposition reactions, since species concentrations are changing, including that of oxygen, and temperature is changing.

The position of the edge of the flame is apparent in the profiles of Figures 9-13, where the fuel species disappear and minima are found in the oxygen concentrations and maxima in the concentrations of the product species. Examination of the profiles for the three flames does not reveal any evidence that water is producing direct chemical changes that can be related to soot formation.
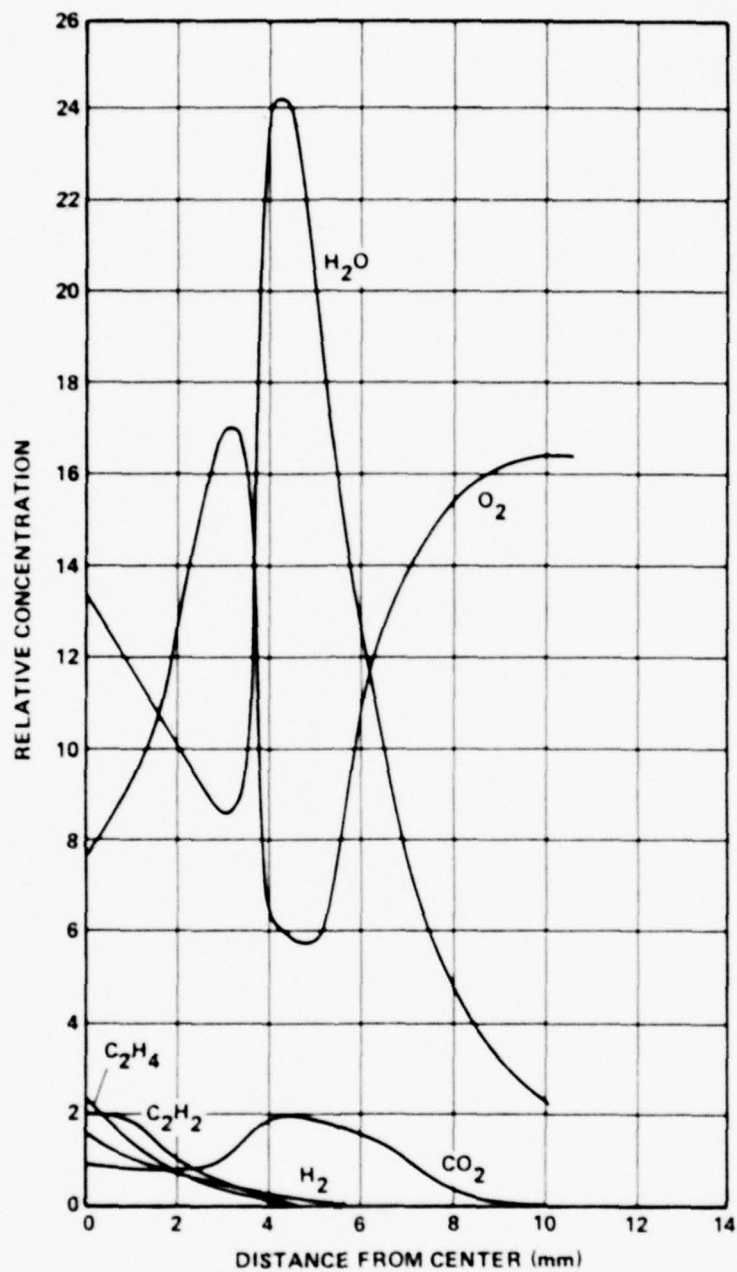
25

Figure 12. Horizontal Profiles of Various Species 1.5 cm above the Burner in a C_2H_4-H_2O/Air Diffusion Flame.
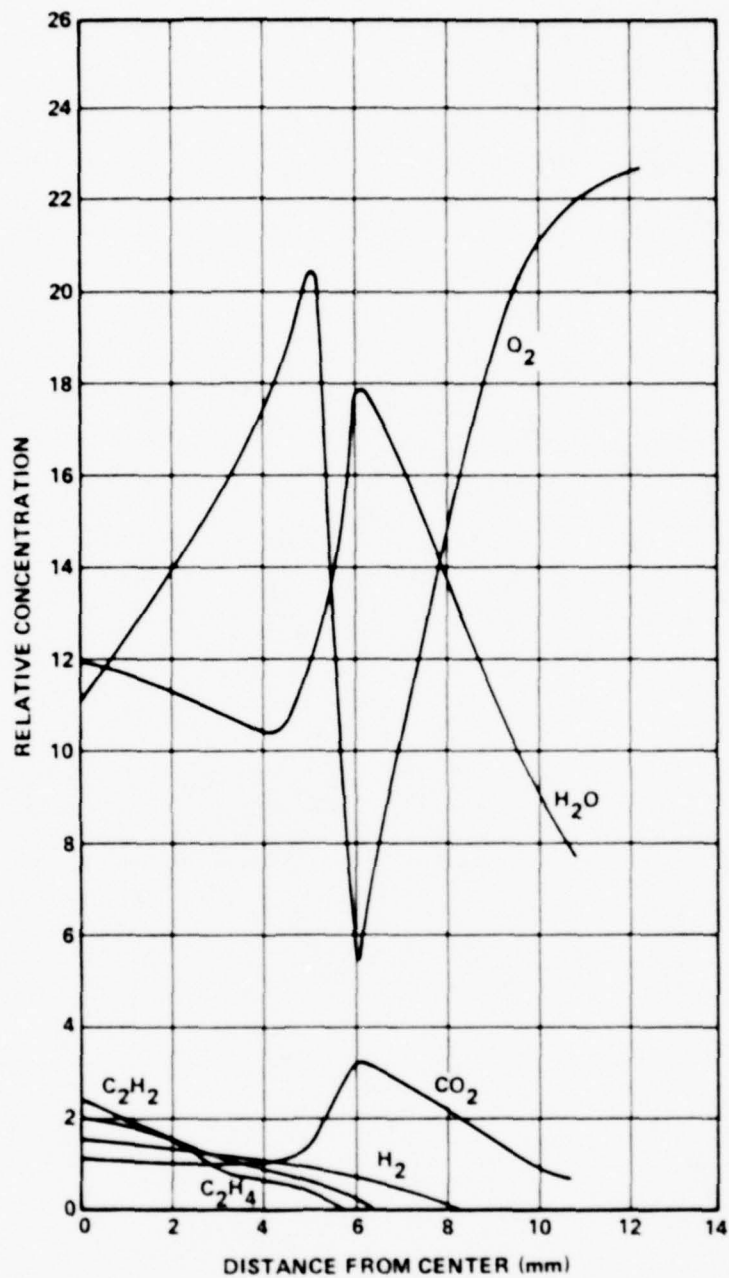
Figure 13. Horizontal Profiles of Various Species 1.5 cm above the Burner in a C_2H_4-N_2/Air Diffusion Flame.

There is another point to mention in connection with the species profiles. The concentration of CO was not measurable since the oxidizer was air (future plans call for using an O_2/argon mixture as oxidizer). However, the important heat-releasing reaction:

$$CO + 1/2 \; O_2 \rightarrow CO_2 \qquad\qquad (10)$$

is the step whereby carbon dioxide is being produced.

Not included in the profiles are some species which were present in observable but not accurately measurable amounts, their concentrations being of the order of less than 0.1 on the relative scale. The species considered were seen in all three flames. If a difference in concentration of any occurred in any of the flames, this fact was obscured by the overall low amounts. At 0.5 cm above the burner, along the central axis, the mass spectrometric traces showed the presence of 1,3 butadiene and somewhat less diacetylene. At 1.5 cm, the diacetylene concentration had increased while the butadiene had all but disappeared. A trace of vinyl acetylene (CH_2=CH-C≡CH) also seemed to be present at both heights. Above the 1.5 cm level, none of these hydrocarbons was seen. At no time was benzene or any other aromatic species observed.
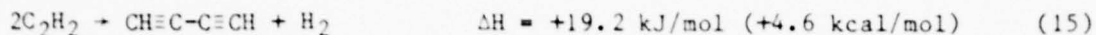
These findings indicate that a small percentage of the ethylene rather than undergoing pyrolysis to acetylene and hydrogen may react to form 1,3-butadiene:

$$2C_2H_4 \rightarrow CH_2\text{=}CH\text{-}CH\text{=}CH_2 + H_2 \qquad \Delta H = +5.4 \text{ kJ/mol } (+1.3\text{kcal/mol}) \qquad (11)$$

Dehydrogenation may then follow:

$$CH_2\text{=}CH\text{-}CH\text{=}CH_2 \rightarrow CH\equiv C\text{-}CH\text{=}CH_2 + H_2 \qquad \Delta H = +194.6 \text{ kJ/mol } (+46.5 \text{ kcal/mol}) \qquad (12)$$

$$CH\equiv C\text{-}CH\text{=}CH_2 \rightarrow CH\equiv C\text{-}C\equiv CH + H_2 \qquad \Delta H = +168.2 \text{ kJ/mol } (+40.2 \text{ kcal/mol}) \qquad (13)$$

An alternative explanation for the formation of the acetylene compounds would involve C_2H_2 itself:

$$C_2H_2 + C_2H_4 \rightarrow CH_2{=}CH{-}C{\equiv}CH + H_2 \qquad \Delta H = +25.5 \text{ kJ/mol} \ (+6.1 \text{ kcal/mol}) \qquad (14)$$

$$2C_2H_2 \rightarrow CH{\equiv}C{-}C{\equiv}CH + H_2 \qquad\qquad \Delta H = +19.2 \text{ kJ/mol} \ (+4.6 \text{ kcal/mol}) \qquad (15)$$

While these latter reactions are attractive steps because they are less endothermic, it should nevertheless be borne in mind that the production of the reactant C_2H_2 from C_2H_4 is also endothermic by 174.5 kJ/mol (41.7 kcal/mol).

Further growth to higher molecular weight unsaturates may have occured but was not observable in the present system. No measurable difference in the kind or concentration of these minor species, which could be soot precursors, were observed with or without water addition.

D. Measurement of Soot

Soot profiles for the neat, water-added and nitrogen-added diffusion flames are shown in Figures 14, 15 and 16, respectively. An important result of the study was the development of the rapid method of soot collection and measurement that is described in the Appendix.

Probings for soot, aside from the four heights shown, were also attempted at 0.5 and 3.6 cm above the burner, but no soot existed at those levels in any of the three flames. Contour drawings representing soot flux in two dimensions for the three flames are shown in Figure 17.

In the middle of the dark zone, about 1.5 cm above the burner, a tarry substance was seen to form on the probe. There is little or no soot present in this region (although there is abundant soot in the luminous zone surrounding the dark zone at this height). Tar formation starts at about 1 cm above the burner, reaching a maximum at about 1.5 cm. Higher in the dark zone the tar disappears and is replaced by soot. Attempts to characterize the tar itself by infrared spectroscopy has so far proven unsuccessful. It is important to note that the tar does not appear to be a precursor to soot, but rather a separate and unrelated material. At any given point in a flame, tar is found or soot is found but never (except in a small overlap region) both together.
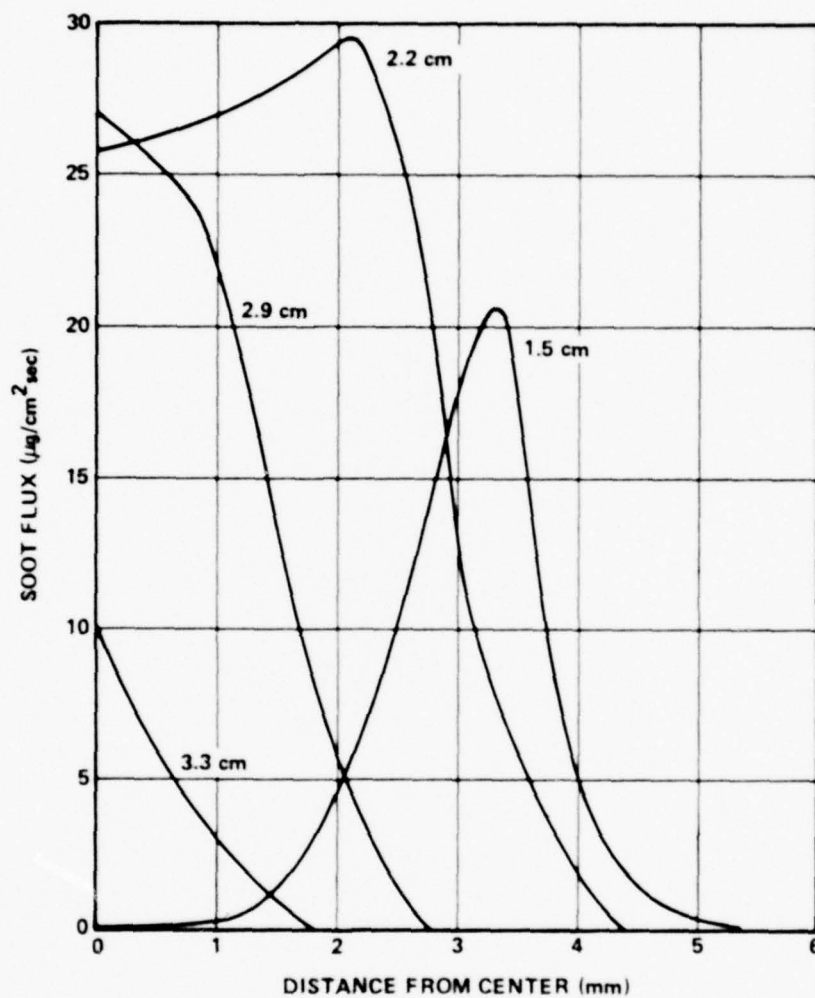
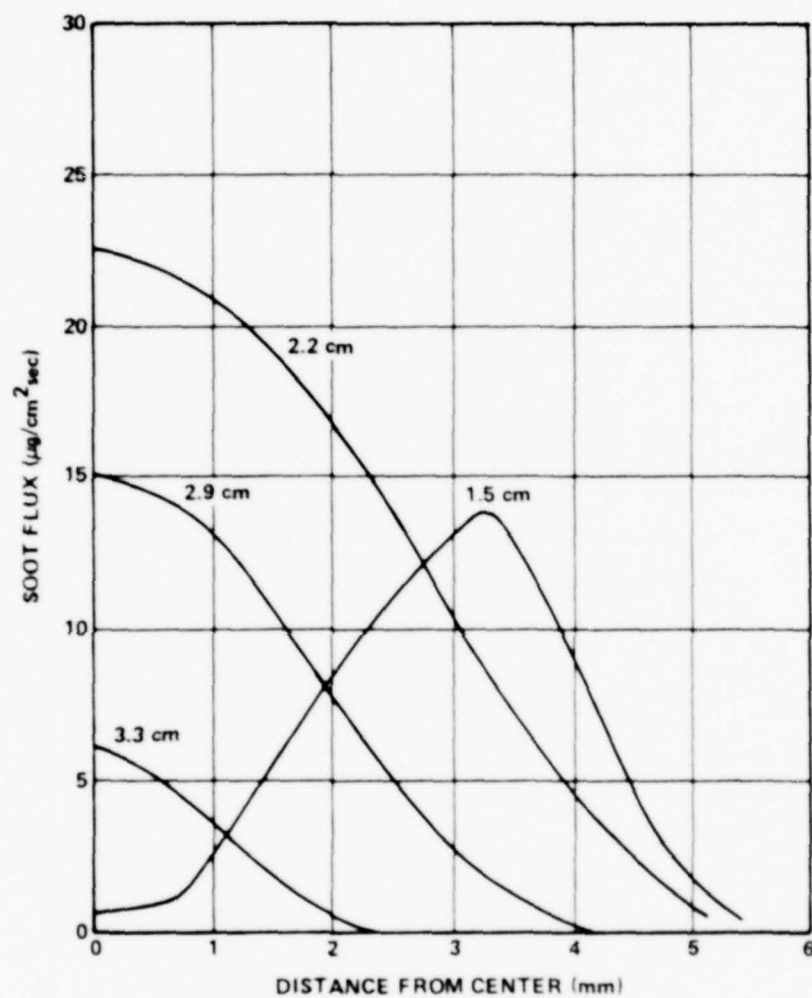Figure 14. Soot Flux Profiles for C_2H_4/Air Diffusion Flame at Various Heights above the Burner.

Figure 15. Soot Flux Profiles for C_2H_4-H_2O/Air Diffusion
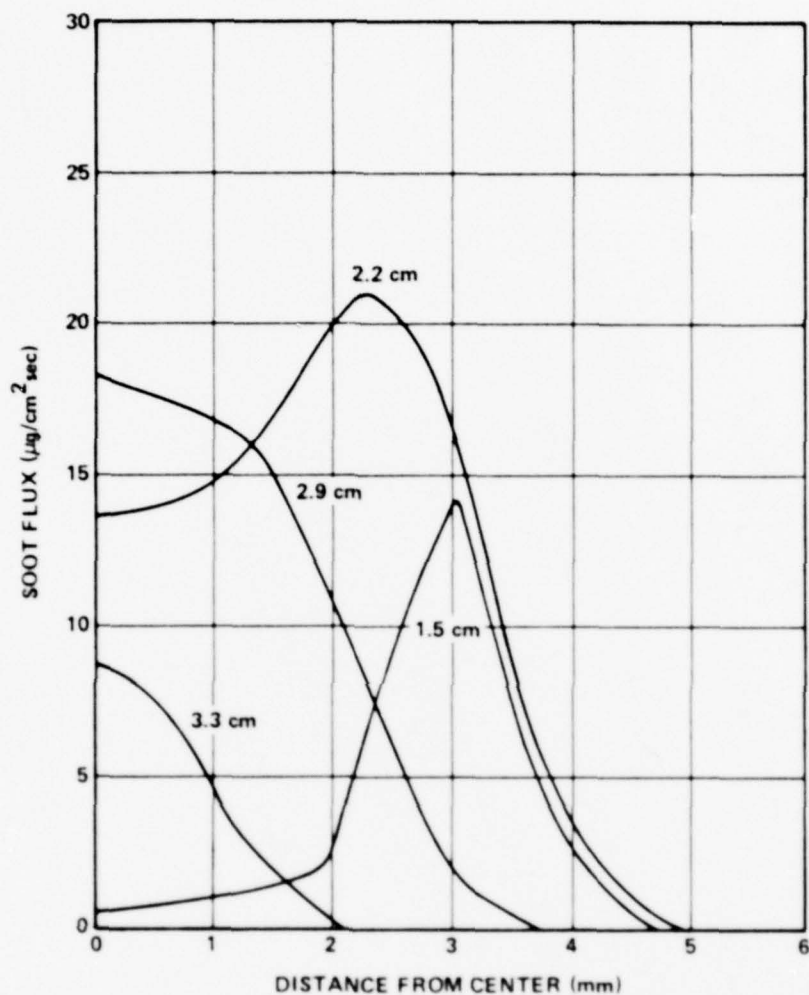Flames at Various Heights above the Burner.

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Figure 16. Soot Flux Profiles for $C_2H_4 \cdot N_2$/Air Diffusion Flames at Various Heights above the Burner.

32

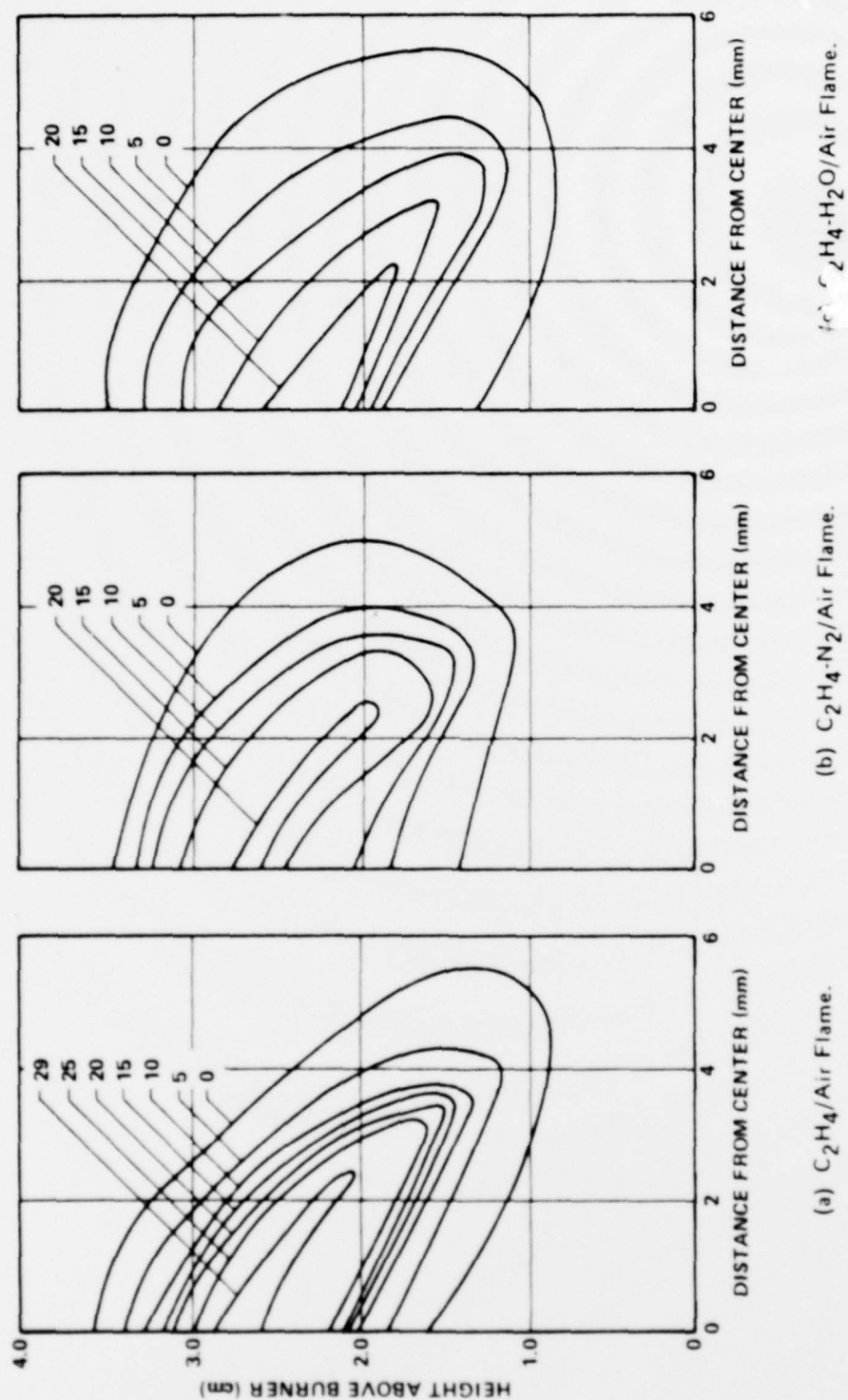Figure 17. Soot Flux Contours for Various Diffusion Flames ($\mu g\ cm^{-2} s^{-1}$).

(a) C_2H_4/Air Flame.

(b) C_2H_4-N_2/Air Flame.

(c) C_2H_4-H_2O/Air Flame.

Soot reaches a maximum concentration at the top of the dark zone and gradually decreases in concentration through the luminous region until it disappears just at the flame top.

Examining the soot profiles for the three flames and the contour diamgrams, it is apparent that there is less soot formed in the water- and nitrogen-added flames than in the neat flame. Any difference between the water- and nitrogen-added flames, however, is not so obvious.

One way of providing a measure of the effect of additives in altering soot is by comparison of soot formation rates through flames. The rates can be obtained by the following procedure:

Plots such as those of Figures 14, 15, 16 represent profiles horizontally through a flame. From many of such profiles (there are four shown in each figure but 15 or 20 may be needed for accuracy) vertical profiles in the direction of gas flow can be obtained. These will be essentially soot flux (in g/cm^2 sec) as ordinate versus vertical height above burner as abscissa, at any lateral position. Consider two points A and B along a vertical traverse separated by a distance L in a sooty part of the flame. The flux at B is F_B; the concentration at B (g/cm^3) is $[c_B] = F_B/v_B$, where v_B is the linear gas velocity at B. Similarly at A the same relations apply so that

$$\frac{F_B}{v_B} - \frac{F_A}{v_A} = \text{concentration increase (or decrease) of soot during residence time in L}$$

or

$$\frac{\frac{F_B}{v_B} - \frac{F_A}{v_A}}{L/\bar{v}} = \frac{\Delta[c]}{L/\bar{v}}$$

where

$$\bar{v} = \frac{v_B + v_A}{2}$$

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and

$$R = \frac{dc}{dt} = \left(\frac{F_B}{v_B} - \frac{F_A}{v_A} \right) \frac{\bar{v}}{L}$$

where R is called the rate of formation of soot but represents the rate of change of soot concentration. Values of v_A, v_B, v_C..., can be obtained with sufficient accuracy by correcting v_o for density change.

Figure 18 represents a plot of R versus height above the burner along the central axis of the neat flame. Temperature and time along this axis are also included. The plot is drawn using only the four data points for soot flux plus two additional points where soot concentration is zero, resulting in only five intervals. These are insufficient to produce accurately a soot formation curve; accordingly, Figure 18 is presented only as an illustration of the method and is not accurate at this time. Further experiments are planned for the future in which soot sampling will be done at much closer intervals.

CONCLUSIONS

1) Water when added to fuel results in a reduction of soot during combustion. The chemical aspect of this process was investigated in a gaseous diffusion flame, using ethylene as the fuel, to attempt to learn the mechanism. Although the study is not entirely complete, it appears at this point that the role of water is to lower temperature throughout the dark zone of diffusion flames, thereby reducing the rate of formation of soot.

2) The comparative effects of water and nitrogen were examined in the flame and it was found that when an amount of water is added that should produce a thermal effect equivalent to that of nitrogen, a much greater reduction in temperature occurs instead. This was attributed to chemical inhibition by water of some exothermic process. The exact reaction cannot be identified because oxidation of C_2H_4, C_2H_2, H_2 and CO is occurring simultaneously in the system.

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RATE OF SOOT FORMATION ($\mu g/cm^3 s$)
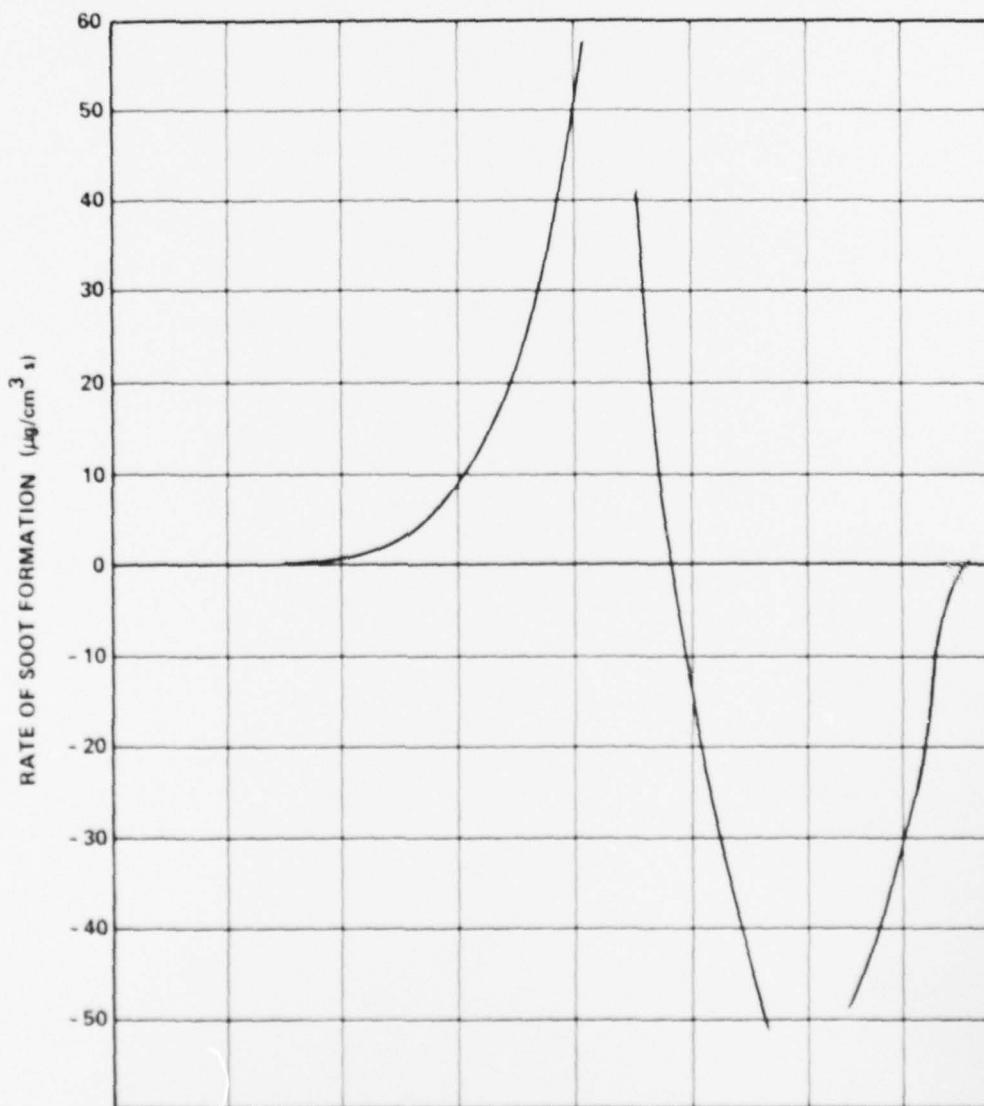
HEIGHT ABOVE BURNER (cm)	0.5	1.0	1.5	2.0	2.5	3.0	3.5
TEMPERATURE ($^{\circ}$K)	1112	1140	1180	1225	1325	1935	1840
TIME (sec)	0.25	0.41	0.56	0.71	0.85	0.96	1.05

3) High concentrations of molecular oxygen were found to be present in the fuel zone of the diffusion flame. Based on calculations and comparison with other studies, the presence of the oxygen was attributed to diffusion of air through the dark zone above the rim of the burner.

4) A new method of sampling soot has been developed in the course of the study. The technique allows rapid and reproducible measurment of mass flux profiles of soot through a flame.

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APPENDIX I

Sampling of Soot in Diffusion Flames

SAMPLING OF SOOT IN DIFFUSION FLAMES

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In the course of an experimental study of the role of water in suppressing flame carbon, we have developed a rapid and reproducible method for quantitatively measuring soot throughout diffusion flames. The overall findings concerning the effect of water will be reported in the future upon completion of the study. In this note we wish to briefly describe the soot sampling technique.

The rationale for performing the overall study derives from the fact that when fuel oil containing added (emulsified) water is burned, substantial reduction in soot emission is realized. A physical process known as "micro-explosion" seems to be at least partly responsible for the effect, which process is being studied by others (1). In addition, it appears that some chemical change may also be partly responsible. Water molecules may attack *soot precursors*, or water may act by reducing the temperature field in the region of soot formation, or it may act by some other mechanism (several have been speculated on). To eliminate the physical part of the process in order to allow only the chemical effect to be investigated, we have chosen a gaseous laminar diffusion flame for study. Complete flame structure will eventually be measured including profiles of chemical species and temperature as well as soot flux. To date only ethylene has been used, in order to establish the technique, although plans call for other fuels in the future. The results given here refer to flames that contain no added water vapor.

A diffusion flame burner was constructed that consists of a thin-walled tube of approximately 20 mm inside diameter which carries the fuel. This is surrounded annularly by another tube of 135 mm inside diameter through which air flows, and which is packed with a series of gauze layers and fine mesh screens. There is a very short chimney of 80 mm diameter positioned on top of the air tube, which extends a short distance below the rim of the fuel tube. The burner produces a steady flame which exhibits no perceptible flickering except at the tip. Ethylene flow rates are typically below

1 cm/sec and air flow is of the order of 10 cm/sec through the chimney, both being controlled by critical orifices.

The technique for measuring soot profiles consists of rapidly inserting a long narrow sliver of glass into the flame for a known length of time at a known height above the burner rim. The glass probe is about two millimeters wide and about seven cm in length. Slices cut off the edge of a microscope slide work well. The combined time to insert and withdraw the glass is of the order of 0.1 to 0.2 seconds. Residence times of the probe in the flame are in the range of two seconds during a test. The glass probe is attached to a mechanical device for insertion and withdrawal. As the probe enters and exits from the flame, a microswitch is activated which is connected to a timer. The exact location in the flame where the probe is positioned during sampling is regulated by a micromanipulator.

When the glass probe emerges from the flame it contains a gradation of deposited soot on its surface which corresponds to the varying soot concentrations in the flame. When the sliver is scanned with a densitometer, optical density readings are obtained whose intensity varies with the soot deposit. The technique is highly reproducible and can be calibrated to yield soot flux rates.

Data from a calibration test are shown in the plots of Figure 1. What one wants to obtain from the type of soot sampling method described here are mass flux profiles through the flame (in two dimensions). In order to obtain these, the following procedure is used. Known amounts of soot are collected from the flame and weighed. This is done using a relatively large probe which can be inserted into the flame at any position and for a time long enough to obtain a weighable sample. (The amount of soot deposited on a glass sliver in two seconds is too little to be weighed.) Figure 1a is a plot of weight of soot collected as a function of time. Next, known amounts of this soot are dispersed over a known area and optical density measurements taken with a densitometer. A convenient way to obtain a uniform dispersal is to place a known weight of soot into water containing a surfactant and treat the dispersion with an ultrasonic probe. (Several

surfactants were tried and Tamol SN, a sodium aryl sulfite, was found to be the most satisfactory.) Figure 1b shows a calibration of optical density versus weight per unit area obtained by this method. The time period of ultrasonic treatment and the soot/H_2O ratio have each been varied by an order of magnitude with no significant change in calibration curves such as that of Figure 1b.

The optical density measurements of soot deposits on thin glass probes are compared with a calibration curve. The optical density varies along the length of a glass probe corresponding to varying soot concentration laterally through a flame at any given height. The amount of soot deposited depends on the length of time the probe resides in the flame. In Figure 1c optical density data are shown for probes inserted for varying lengths of time at 1.50 cm above the burner rim. The data in the figure correspond to the point of maximum soot deposit on each probe.

The entire gradation of deposited soot is measured along probes which were inserted at various heights through the flame. The results represent the varying mass flux of soot. In Figure 2, two flux profiles are presented corresponding to 1.50 and 2.20 cm above the burner rim. Each curve represents an average of about six probings. The resolution of the densitometer was approximately 0.5 mm. Plots such as those shown in Figure 2 require many individual measurements; however, these can be made fairly rapidly.

Tar is also produced in the flame and it deposits on the glass probes when sampling is done low in the flame. However, tar and soot do not occur together except in very small regions of the dark zone. A correction must be made for the optical density of the tar in order to obtain the true soot profile. Because the tar and soot deposits essentially do not overlap, the correction is not difficult to do since the soot wipes off the probe easily, leaving the tar. This correction is relatively small and only applies in the lower part of the central region of the flame.

The sampling method reported here does not overcome any of the uncertanties associated with collecting soot by insertion of a cold surface into a flame. The procedure is probably as accurate as other techniques such as collecting soot on a flat probe and weighing (2), or withdrawing samples by suction through a hollowed probe and oxidizing to CO_2 (3). The advantage of the present method is that a complete mapping of a flame can be accomplished rapidly.

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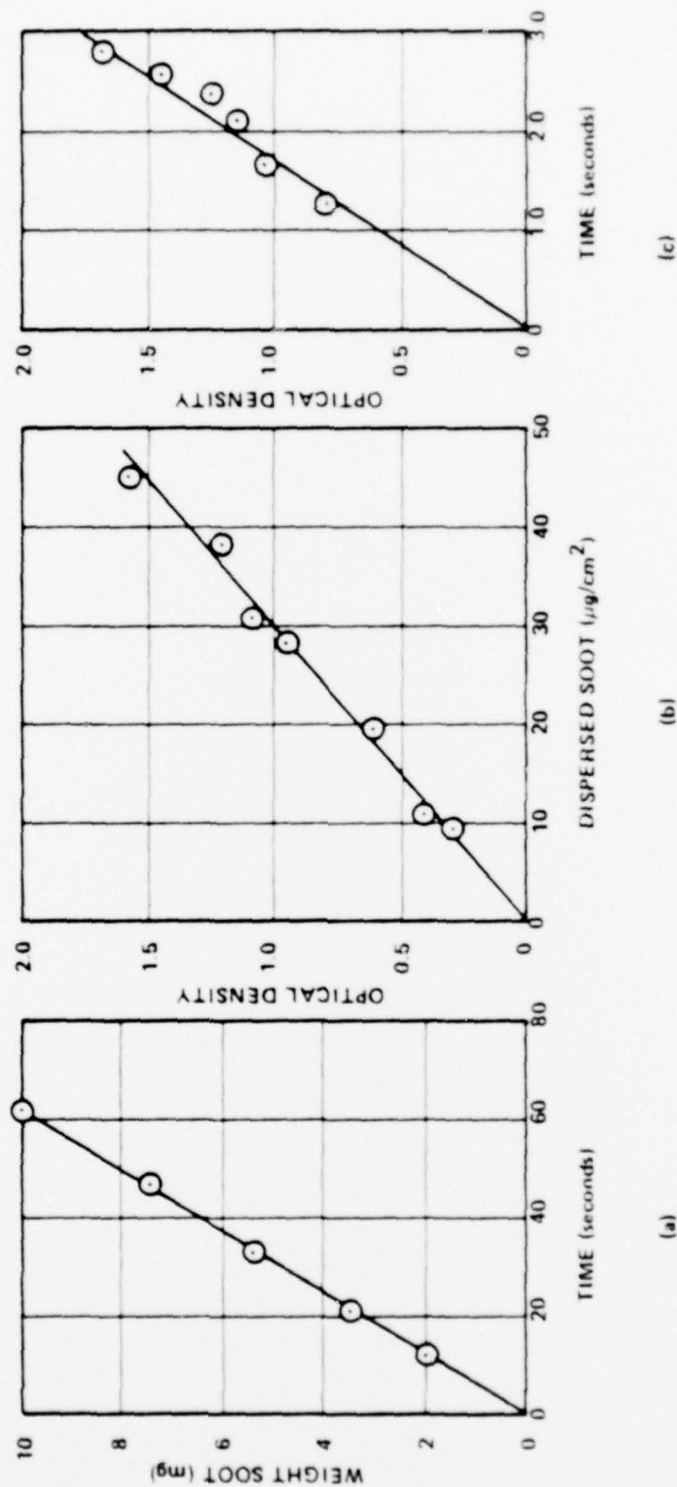3. Fenimore, C. P., and Jones, G. W., Combustion and Flame, 13, 303 (1969).

Figure 1. Plots Illustrating Calibration Data for Soot Sampling Method. (a) Weight of Soot Collected from Ethylene Diffusion Flame as Function of Time. (b) Optical Density Measurements for Various Amounts of Soot Dispersed over Known Areas. (c) Optical Density Measurements for Soot Deposited at One Point on Glass Probe as Function of Residence Time in Flame (1.5 cm above Burner Rim).
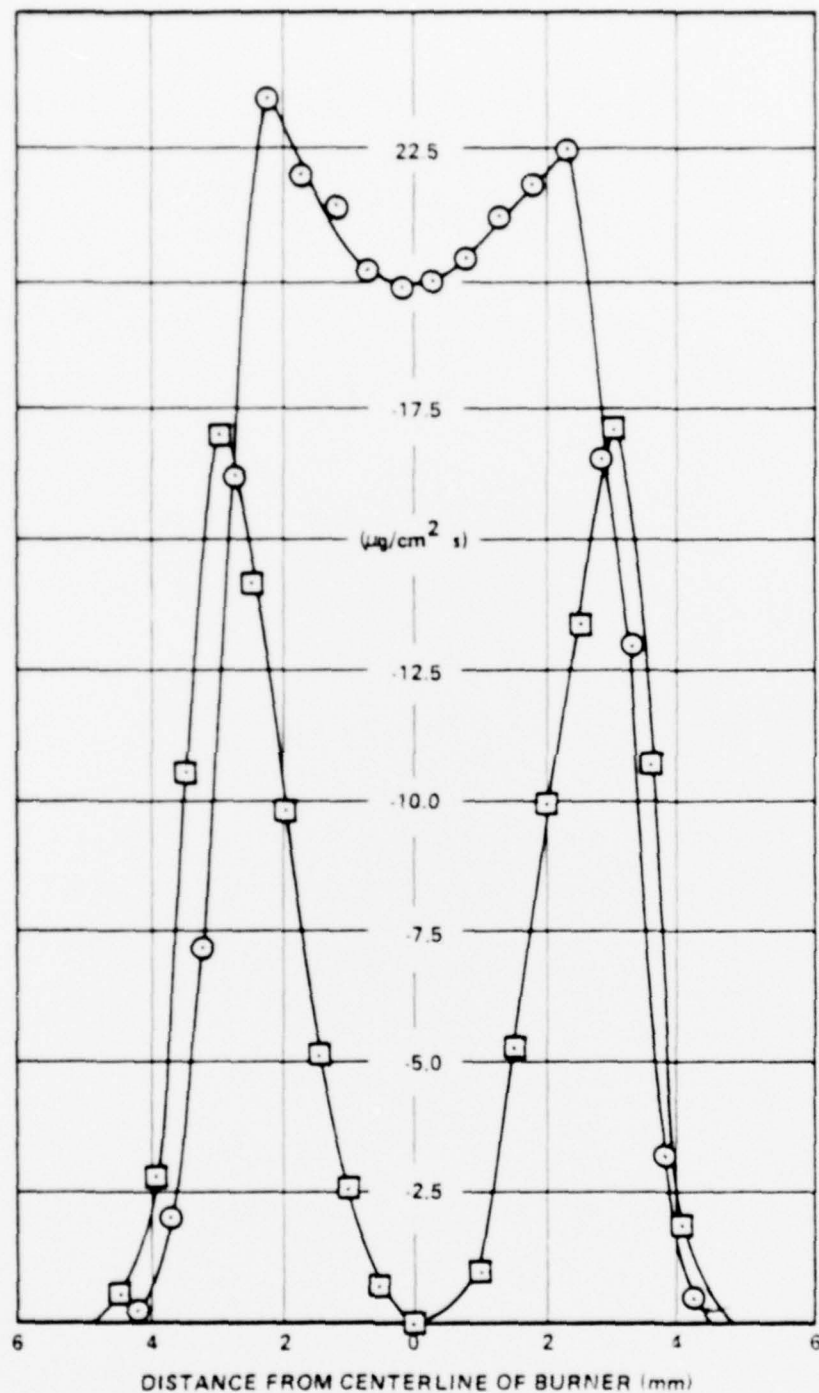
Figure 2. **Mass** Flux Profiles of Soot in an Ethylene Diffusion Flame.
⊙ 2.20 cm; ⊡ 1.50 cm above Burner Rim.