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FINAL TECHNICAL REPORT

CHEMISTRY OF COMBUSTION OF FUEL-WATER MIXTURES

Submitted by:

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Submitted to:

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Director, Power Program
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Attn: Mr. James R. Patton, Jr.
Code 473

Ref: Contract N00014-80-C-0534

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ATLANTIC RESEARCH CORPORATION
ALEXANDRIA,VIRGINIA · 22314

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ABSTRACT

The continuation of an experimental flame study concerning the nonphysical processes that lead to soot suppression when water is added to fuel, begun in a previous program (1), is reported. The study included a mapping of temperature, chemical species and soot profiles of laminar diffusion flames with and without water added. Fuels studied included ethylene and a benzene/hydrogen mixture. Flames with nonreactive gases added (argon, nitrogen) were also studied for comparison purposes.

The study concludes that the reduction of soot by water in an ethylene diffusion flame can be completely explained by thermal effects. The results are not as definitive for benzene. The addition of water causes a greater reduction in soot than does a thermally equivalent addition of argon, but no noticeable differences in chemical species profiles are observed. There is evidence, however, that water addition causes an increase in concentration of an oxygen-containing tarry substance present in the flame prior to soot formation.

During the course of the study it was also possible to estimate both soot particle diameters (1-2 x 10^{-6} cm at the beginning of the oxidation zone) and an activation energy for soot oxidation by the OH radical (7-8 kcal/mole). In addition, it was possible to confirm the presence of and quantify the oxygen concentration in the center of diffusion flames, first reported under the previous program (1).

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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. This study is a continuation of a program performed under a previous contract with ONR (Contract No. N00014-78-C-0649). The final report for that contract (1) contains a discussion of the soot formation process, and the reader is referred to that report for the details of what is now summarized here.

The burning of hydrocarbon fuels is often 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. Release of free soot is almost never desirable in a combustion process.

A good measure of the sooting tendency of a fuel is the 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. Several papers (6-9) presented at the recent General Motors Symposuim on particulate combustion augment the older information.

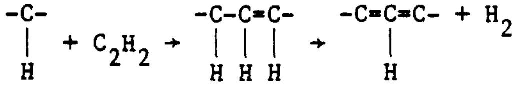
The nature of soot formed in flames is independent of the type of fuel used or the conditions under which the fuel is burned. Physically, soot consists of spherical particles with dimensions of the order of several hundred Angstroms. These spheres are usually attached to each other so as to form what looks like a string of beads, with larger agglomerates that form what look like clusters of grapes. The individual spheres themselves were at one time thought to be made up of graphite-like crystallites with dimensions of the order of a few tens of Angstroms; more recently evidence suggests that the spheres are comprised of concentric shells.

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:

Naphthalenes > Benzenes > Acetylenes > Diolefins > Monolefins > Paraffins (10).

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, 1,3 butadiene, C_6H_5 and positive ions ($C_mH_n^+$) (3,5). Several specific mechanisms have been suggested having various degrees of credibility. Porter's theory (4) asserts that acetylene is converted directly to carbon and hydrogen without involving C_2 or any higher hydrocarbon. He considers the key nuclection step to be:



$$\underset{|\atop H}{-C-} + C_2H_2 \rightarrow \underset{\atop H\;\,H\;\,H}{-C-C=C-} \rightarrow \underset{\atop H}{-C=C=C-} + H_2 \qquad (1)$$

Gay, et al. (11), however, found that acetylene decomposes thermally to yield polyacetylenes, i.e., higher hydrocarbons.

$$2C_2H_2 \rightarrow C_4H_3 + H \qquad (2)$$

$$C_4H_3 + M \rightarrow C_4H_2 + H + M \qquad (3)$$

$$C_4H_2 + C_2H_2 \rightarrow C_6H_3 + H \qquad (4)$$

$$C_6H_3 + M \rightarrow C_6H_2 + H + M \qquad (5)$$

etc.

Glassman (12) designates 1,3 butadiene as the primary soot precursor due to its conjugated nature, saying that acetylene cannot be the main precursor because it is not conjugated. Calcote (9) favors ionic mechanisms in the formation of soot, with large positive aromatic ions having mass greater than 300 being the soot precursors.

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 addition. A specific study (13) 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 (14) and Jacques, et al. (15) 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:

1) For liquid fuel, production of carbon could be lessened due to the cooling effect of the water reducing the liklihood of liquid phase pyrolysis.

2) A lowering of the temperature in the fuel rich zone by water would decrease the soot formation rate.

3) Soot after being formed could directly react with water according to the producer gas reaction:

$$C + H_2O \rightarrow CO + H_2 \qquad (6)$$

4) Soot after being formed could be oxidized by the OH radicals formed by the water reacting with hydrogen atoms:

$$H + H_2O \rightarrow H_2 + OH \qquad (7)$$

although this is unlikely as kinetically, atomic hydrogen will preferentially react with the fuel itself, over the range of flame temperature:

$$H + RH \rightarrow H_2 + R \qquad (8)$$

5) Water could react directly with one or more soot precursors. Plausible reactions can be hypothesized which would tend to reduce the level of soot production.

In the present program, it was desired to continue the study of the chemical effects of water independently from the physical, and to determine which chemical effects are responsible for the reduction of soot. The use of gaseous laminar diffusion flames as a means to this study removed the possibility of physical soot reduction by water.

EXPERIMENTAL

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 fuel as well as the water, nitrogen or argon additives where appropriate. The outer tube, measuring 135 mm in diameter carried an argon/oxygen mixture. Both tubes were packed alternately with a series of gauze layers and fine mesh screens, which served to provide laminar flow with a flat profile. 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 specially constructed enclosure which allowed for stabilizing the flame under various conditions as well as allowing for easy interchanging of flame probes. The result was a flame which was visually steady with the exception of occasional slight flickering at the tip.

Two fuels were studied extensively during the course of the contract. Ethylene, the study of which had initiated under the previous program (1), was chosen because it produces a moderate amount of soot, intermediate to fuels such as low sooting methane and high sooting acetylene. Thus an easily measurable, yet not overwhelming amount of soot could be obtained. Benzene was chosen as the second fuel since, being aromatic, it is possible that it would follow a different route to soot formation than would an aliphatic substance. Since benzene produces a profuse amount of soot it was necessary to add both a diluent (argon) and a non-sooting fuel (hydrogen) to the benzene stream so that a sufficiently high flame containing a measurable amount of soot could be established.

CP grade ethylene, prepurified nitrogen, ultra-high purity argon and high purity hydrogen were metered into the burner flow tube when necessary through calibrated critical orifices. The same method was used to meter mixtures of 21% extra-dry grade oxygen and 79% ultra-high purity argon, or compressed air into the outer tube.

In the ethylene 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."

In the benzene experiments, argon was bubbled through a flask containing A.C.S. grade benzene and then mixed downstream with a metered mixture of hydrogen and additional argon. When water was added, the hydrogen-argon mixture was bubbled through the heater water flask.

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

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

Temperature profiles were obtained with a 50 mm Silicone coated Pt/Pt 10% Rh thermocouple connected to a strip chart recorder. Soot buildup on the thermocouple bead was corrected for by extrapolation. The soot could then be either physically knocked off, or burned off by maneuvering the bead into an oxidizing part of the flame before moving on to the next point. Corrections due to radiative cooling of the thermocouple were applied. At the maximum flame temperature (about 2000°K) the correction amounted to about 400°K.

The method used to sample the soot is one that was developed in this laboratory as a part of the previous program (1). A paper describing this method has been published by Combustion and Flame (16). 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 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 (17), the probe was constructed of 3 mm OD quartz tubing tapered at a 20° angle to a 50 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 1.5×10^{-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.

A summary of the species concentrations for the experiments performed appears in Table I.

Table 1. Diffusion Flames Studied in Soot Suppression Experiments

SOOTING FUEL	MASS FLOW g/s	ADDITIVE 1	MASS FLOW g/s	ADDITIVE 2	MASS FLOW g/s	ADDITIVE 3	MASS FLOW g/s	OXIDANT MIXTURE	MASS FLOW g/s	SOOT PROFILE	SPECIES	TEMP.
C_2H_4	2.51×10^{-3}							21% O_2 in Ar	0.43	X	X	X
C_2H_4	2.51×10^{-3}	H_2O	7.00×10^{-4}					21% O_2 in Ar	0.43	X	X	X
C_2H_4	2.51×10^{-3}	N_2	2.37×10^{-3}					Compressed Air	0.43	X		X
C_6H_6	9.56×10^{-4}	H_2	1.42×10^{-4}	Ar	1.38×10^{-2}			21% O_2 in Ar	0.43	X	X	X
C_6H_6	9.56×10^{-4}	H_2	1.42×10^{-4}	Ar	1.90×10^{-2}			21% O_2 in Ar	0.43	X		X
C_6H_6	9.56×10^{-4}	H_2	1.42×10^{-4}	Ar	1.38×10^{-2}	H_2O	1.78×10^{-4}	21% O_2 in Ar	0.43	X		X
C_6H_6	9.56×10^{-4}	H_2	1.42×10^{-4}	Ar	1.38×10^{-2}	H_2O	1.11×10^{-3}	21% O_2 in Ar	0.43	X	X	X
C_6H_6	9.56×10^{-4}	H_2	1.42×10^{-4}	Ar	1.38×10^{-2}	H_2O	6.61×10^{-4}	21% O_2 in Ar	0.43	X		X

RESULTS AND DISCUSSION

A. Ethylene Diffusion Flames

A preliminary study of the effect of water on ethylene diffusion flames was completed under the previous ONR Program (1). At that time, probings were performed as horizontal traverses across the flame at varying heights above the burner. These heights were usually 5-7 mm apart from burner to flame tip. The probings revealed extremely steep gradients in the soot flux in various regions of the flame, and only slightly less steep gradients in temperature and chemical species profiles. In the present study, these experiments have been repeated at each millimeter of vertical distance. This greatly increased the accuracy of the data.

The neat ethylene diffusion flame, produced using a mass flow of 2.51×10^{-3} g/s C_2H_4, appears as a luminous flame 3.6 cm in height. Linear velocity of fuel at this flow rate is 0.77 cm/s. The addition of 0.70×10^{-3} g/s H_2O (mole fraction = 0.302) increases the velocity to 1.10 cm/s, while the addition of 2.37×10^{-3} g/s N_2 (mole fraction = 0.486) results in a velocity of 1.49 cm/s. As expected, neither additive changes the height of the diffusion flame, and each only slightly reduces the luminosity to the naked eye.

Temperature profiles for the three ethylene flames along the central vertical axis appear in Figure 1. The temperature for the water-added flame at 5 mm above the burner is about 150°K lower than that of the neat flame. The temperature of the nitrogen-added flame was set to be equal to that of the water-added flame at 5 mm above the burner by adjusting the N_2 flow. Temperatures for the three flames in this study are quite similar to those found under the previous contract (1) except in the sooting region where they are substantially (200-300°K) higher than in the previous study. It is believed that the current results more accurately reflect the true flame temperatures for two reasons: 1) Sampling every mm of height reduces the need for interpolation, and 2) the use of a strip chart reader gives continuous time-dependent temperature information. This shows a decrease in temperature with buildup of soot deposit. Thus, extrapolation back to $t = 0$, where there is no soot, would result in the actual flame temperature at any position (after radiation cooling corrections are applied.)

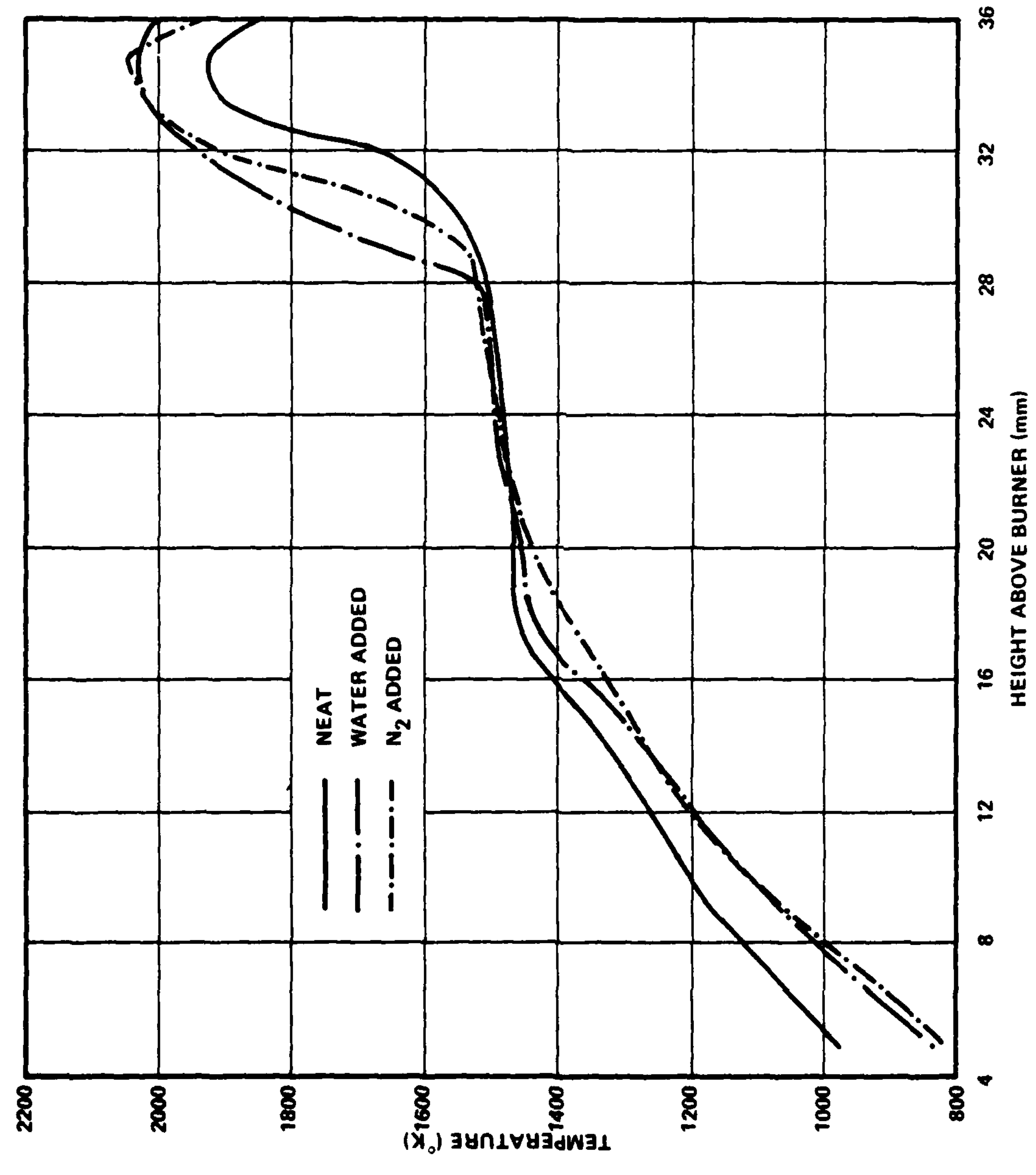


Figure 1. Temperature Profiles for Ethylene Flames – Central Vertical Axis

As stated earlier, the thermocouple bead was coated with a Silicone oil, but comparison with an uncoated bead indicated virtually no difference in the temperature readout.

It should be noted that for the most part, the water-added and nitrogen-added flames parallel one another in temperature up the center line. In the results reported for the previous study for similar amounts of water and nitrogen, the water-added flame exhibited a substantially lower temperature in the dark zone than did the nitrogen-added flame. A comparison of the heat-sink effect for water and nitrogen can be made by choosing a point - say 15 mm above the burner - and comparing the relative temperatures of the two flames. The temperature in both cases is 1300°K. The heat needed to raise the temperature of water from 398° to 1300°K (remembering the water is preheated) is 35.3 kJ (8.5 kcal) (18); for nitrogen from 298 to 1300°K it is 31.4 kJ (7.5 kcal). The water-added flame has 30.2 mole % water resulting in a relative heat sink effect of 0.302 x 35.3 = 10.7 kJ (2.5 kcal), while the nitrogen-added flame contains 48.6 mole % N_2 corresponding to 0.486 x 31.4 = 15.3 kJ (3.6 kcal). On a purely thermal basis, 48.6 mole % nitrogen should reduce the temperature of the neat ethylene flame by a factor of 15.3/10.7 = 1.43 more than does 30.2 mole % of water. The temperature of the neat flame at 15 mm above the burner is 1360°K. If the nitrogen reduces the temperature to 1300°K, a drop of 60°K, then the water should drop the temperature by 42° to 1318°K. This is certainly within the experimental error of the system, and the basically equivalent temperatures of the water-and nitrogen-added flames are essentially correct. Thus, the differences reported in the previous study were probably due to inaccuracies caused by sooting on the thermocouple bead and the fewer data points taken.

Mass spectrographic scans were performed on the neat and water-added flames, again probing at each vertical mm along the central axis. Since argon/oxygen mixtures rather than compressed air were used to support combustion, chemical species profiles could be obtained which are much more complete than those obtained in the earlier study. Profiles for the major species: O_2, H_2, H_2O, C_2H_2, CO_2, CO and Ar for the neat and water-added flames appear in Figures 2 and 3 respectively. The removal of N_2 form the system by using Ar/O_2 rather than compressed air removes a major contributor to the m/e = 28 peak and facilitates the profiling of CO. In addition, the m/e = 40 peak, attributable only to

Ar becomes an excellent tracer of the diffusion process. Since it is now possible to profile all major flame species, concentrations are reported as mole fractions rather than "relative concentrations" as used in the earlier study.

Comparing Figures 2 and 3, there appears to be very little difference in the concentrations of the major species between the neat and water-added flame with the exception, of course, of the higher H_2O concentration in the lower part of the latter. Thus, it would seem that water has no chemical effect on any of the major species present in ethylene flames.

The rapid decay in ethylene concentration moving downstream can be attributed to a large extent to dilution by argon as witnessed by the nearly comparably rapid rise in argon concentration over the same distance. The ethylene decay is also in part due to its pyrolysis to acetylene and hydrogen, as can be seen by the increase in acetylene concentration in the lower part of the flame. It is more difficult to observe chemical buildup and decay of hydrogen because of its tendency to diffuse rapidly.

It would be desirable to determine whether ethylene in the flame is disappearing through pyrolysis or by oxidation. We have attempted some analysis of this question, using data such as reported by Tanzawa and Gardiner (19). Estimations of pyrolysis rates through the concentration and temperature fields early in the flame were made as best as could be done; however, no firm conclusions could be drawn. Essentially, the difficulty lies with a lack of data on required free radical concentrations, which would allow the importance of chain propagating reactions to be assessed. The calculations indicate that ethylene loss is primarily via pyrolysis rather than oxidation; and the presence of C_2H_2 supports this. Secondary fuel reactions are also occurring to produce four-carbon unsaturates as illustrated in equations 9-14 below.

Higher in the flame, oxidation reactions become important, as can be seen by the buildup first of CO and later of CO_2. These reactions will be discussed in a later section in connection with soot oxidation.

The fact that oxygen is present in the fuel zone of diffusion flames which was found in the previous study (1) is reaffirmed here. It is also now possible to be more quantitative because of complete mapping of major species. Oxygen

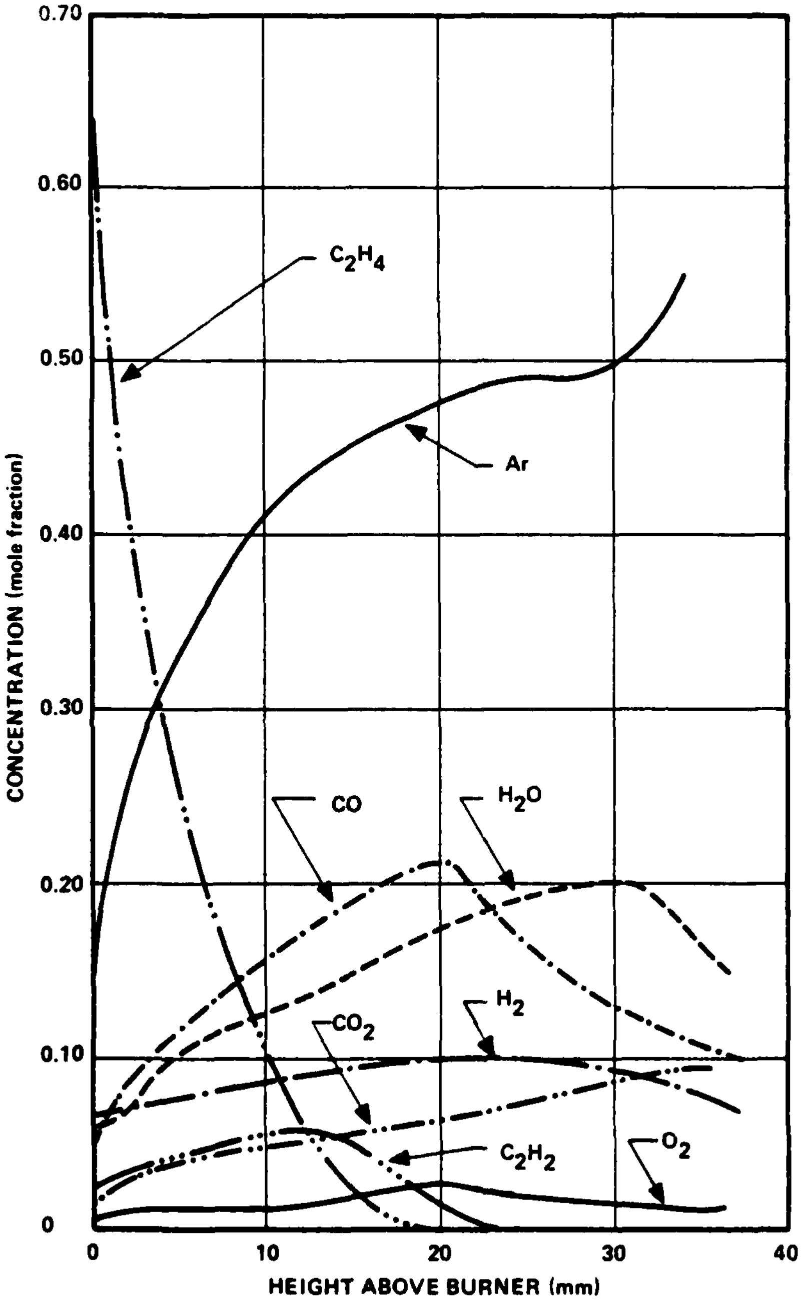


Figure 2. Mole Fractions of Major Species Neat Ethylene Flame - Central Vertical Axis

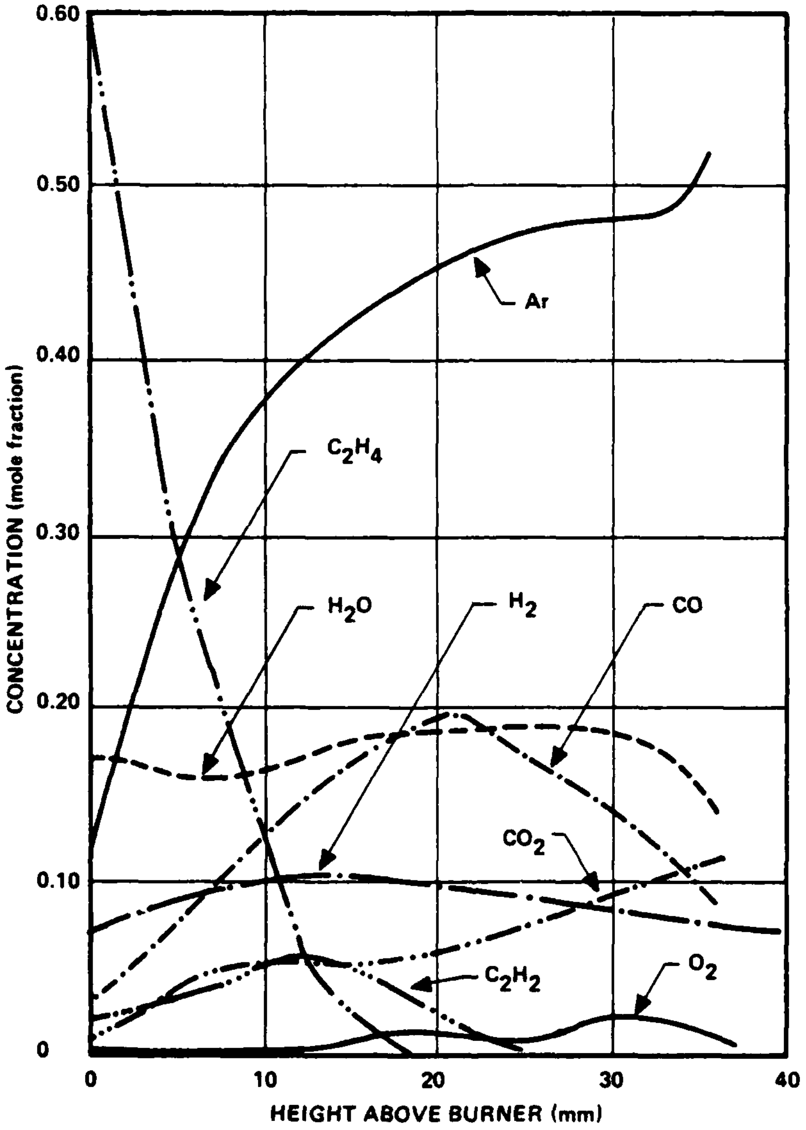


Figure 3. Mole Fractions of Major Species for Water-Added Ethylene Flame - Central Vertical Axis

is generally present in amounts of from 0.5 - 2.5 mole percent with maximum concentration 5-10 mm below the flame tip.

The explanation for the presence of oxygen in the fuel zone has already been presented in the previous report. It involves the diffusion of oxygen (and in this case, argon) through the flame quenching zone just above the burner rim. The explanation showed that an estimated oxygen diffusion rate would be comparable with the fuel flow rate. At the time of the last report, references were cited (20,21) indicating that this phenomenon had been observed by others, although those observations were more alluded to in the other studies than actually stated. More recently, however, there have been at least two reports (22,23) in which the presence of oxygen in the fuel zone of diffusion flames has been discussed. Both the quantities of oxygen and the explanation derived in this laboratory are compatible with these other observations.

In addition to the major species already discussed, three other hydrocarbons could be identified as minor components existing for short periods of time within the flame. These species are 1,3 butadiene, diacetylene and vinyl acetylene. All three were observed under the previous study and discussed at that time. Since in the present study the flames were probed every millimeter, it is possible to describe the buildup and decay of these species at least to a first approximation. The most abundant of these species is diacetylene which in the neat flame builds to a maximum of perhaps 0.3 mole % between 10 and 15 mm above the burner, and is gone by 20 mm. Vinyl acetylene maximizes at about 0.25 mole % at 10 mm and has totally disappeared at 17 mm. 1,3 butadiene is also at its maximum concentration (about 0.15 mole %) at 10 mm and disappears above 14 mm. The concentrations are admittedly somewhat estimated because of inaccuracies incurred on measuring such small m/e peaks. The concentrations in the water-added flame for all three species are somewhat lower, but achieve maxima at the same relative height above the burner. Diacetylene maximizes at about 0.2 mole %, vinyl acetylene at about 0.15 mole % and 1,3 butadiene at about 0.1 mole %. Concentration profile estimates for these three species for both flames are combined in Figure 4. 1,3 butadiene can form by the reaction of two ethylene molecules:

$$C_2H_4 + C_2H_4 \rightarrow CH_2 = CH - CH = CH_2 + H_2 \qquad (9)$$

or by the reaction of ethylene with acetylene

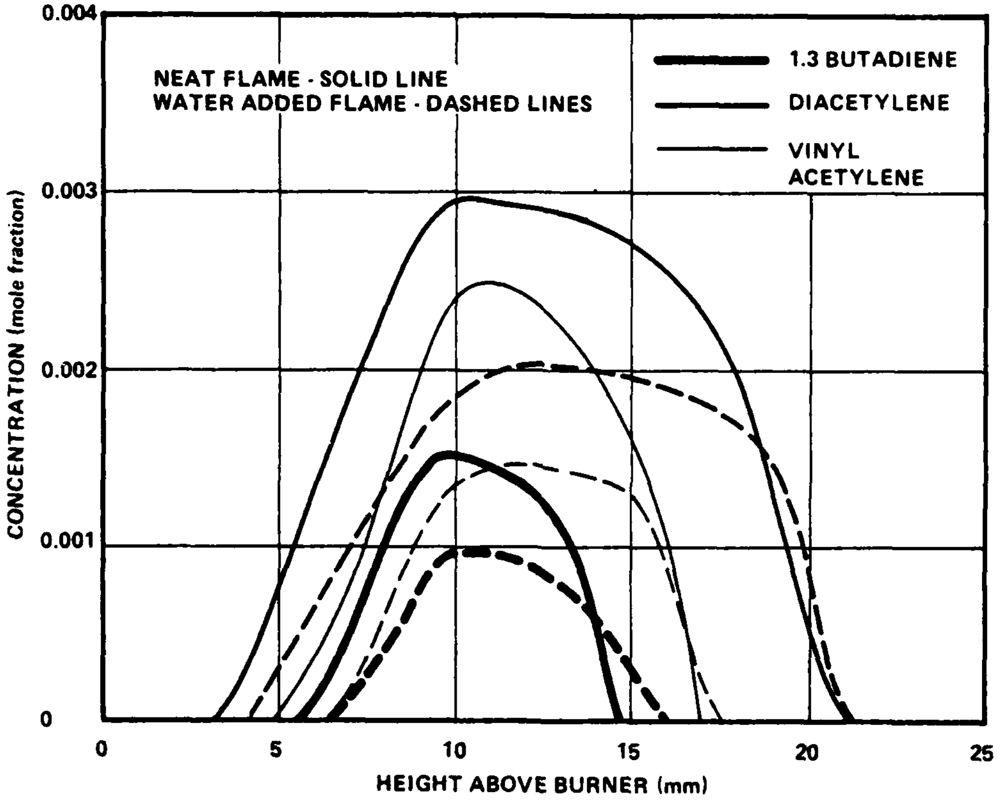


Figure 4. Minor Species Profile Estimates for Neat and Water-Added Ethylene Diffusion Flames - Central Vertical Axis.

$$C_2H_4 + C_2H_2 \rightarrow CH_2 = CH - CH = CH_2 \qquad (10)$$

Vinyl acetylene can also be produced from ethylene and acetylene

$$C_2H_4 + C_2H_2 \rightarrow CH \equiv C - CH = CH_2 + H_2 \qquad (11)$$

or from dehydrogenation of 1,3 butadiene

$$CH_2 = CH - CH = CH_2 \rightarrow CH \equiv C - CH = CH_2 + H_2 \qquad (12)$$

The dehydrogenation can proceed further to form diacetylene:

$$CH \equiv C - CH = CH_2 \rightarrow CH \equiv C - C \equiv CH + H_2 \qquad (13)$$

Diacetylene can also be produced directly from acetylene:

$$C_2H_2 + C_2H_2 \rightarrow CH \equiv C - C \equiv CH + H_2 \qquad (14)$$

The lower concentrations of these three species in the water-added flame can probably be attributed to a thermal effect. The lower temperature in the lower part of the water-added flame would inhibit all of these endothermic reactions. At the same time, the lessening of ethylene and acetylene decay (since less of these are being used to produce the minor species) would be so small (of the order of a 1% difference) that it could not be observed. The possibility that one or more of these minor species reacts with water exists but no reaction products could be observed.

Further growth of the three minor species to higher molecular weight unsaturates, conceivably a route to soot, may have occurred but again was not observable. At no time was benzene or any other aromatic species found in the system.

A major increase in accuracy of this study over the previous one occurred in the measurement of soot profiles. By injecting the soot probes into the flame at each mm of flame height, it was possible to obtain a workable representation of soot formation and oxidation. (In fact, if all the soot probes are placed edge-to-edge in the correct order an instantaneous "picture" of soot formation and oxidation for that particular flame is obtained. Such a picture is shown for the neat ethylene flame in Figure 5.) In addition to the soot, a tarry substance is seen to form on the probe at positions below where soot forms. This phenomenon, already noted during the previous program, will be discussed in the section on benzene.

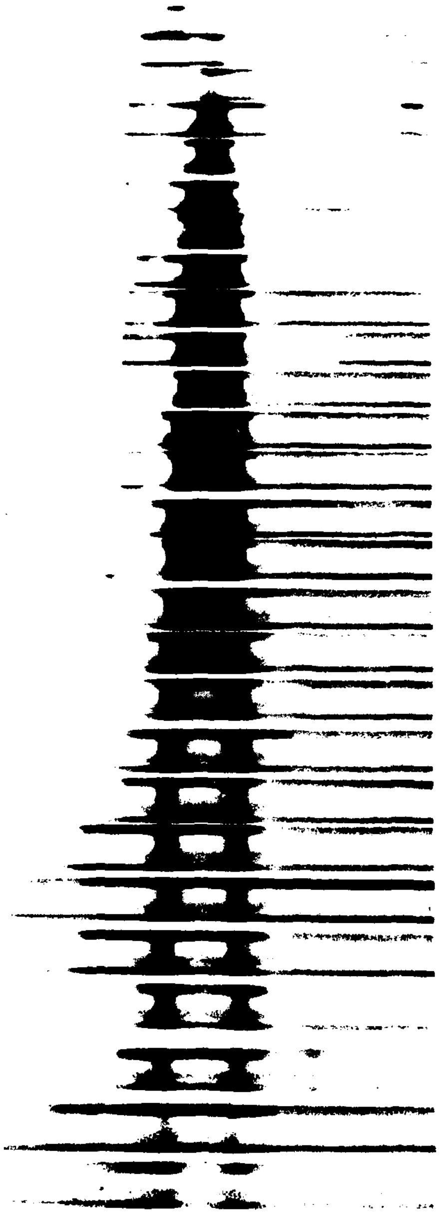


Figure 5. Soot Deposits on Probes Inserted Into an Ethylene Diffusion Flame at Each Millimeter of Height.

Soot production for the water- and nitrogen-added flames is quite similar in quantity and roughly one-third lower than that for the neat flame. Soot flux profiles up the center line for the three flames appear in Figure 6. These profiles reproduce the basic forms of the cruder soot profiles for the three flames studied in the previous program with reasonable accuracy. The fact that a data point was obtained at each mm reduced the need for interpolation and allowed the construction of reliable soot formation rate curves. Such curves can be derived from the center line concentration profiles as follows: Consider two points, A and B, along the central vertical axis 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

$$\frac{F_B}{v_B} - \frac{F_A}{v_A} = \text{Concentration increase (or decrease) of soot during residence time in L} \qquad (15)$$

or

$$\frac{\dfrac{F_B}{v_B} - \dfrac{F_A}{v_A}}{L/\bar{v}} = \frac{\Delta[c]}{L/\bar{v}} \qquad (16)$$

where

$$\bar{v} = \frac{v_B + v_A}{2} \qquad (17)$$

and

$$R = \frac{dc}{dt} = \left(\frac{F_B}{v_B} - \frac{F_A}{v_A}\right)\frac{\bar{v}}{L} \qquad (18)$$

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, the initial linear gas velocity, for density change. Soot formation rate profiles for the three flames, derived by means of the above argument, are presented in Figure 7. These profiles actually reflect both soot formation and oxidation rates for the three flames. Again, the water-added and nitrogen-added flames appear to parallel one another, while the neat flame exhibits much greater formation and oxidation rates.

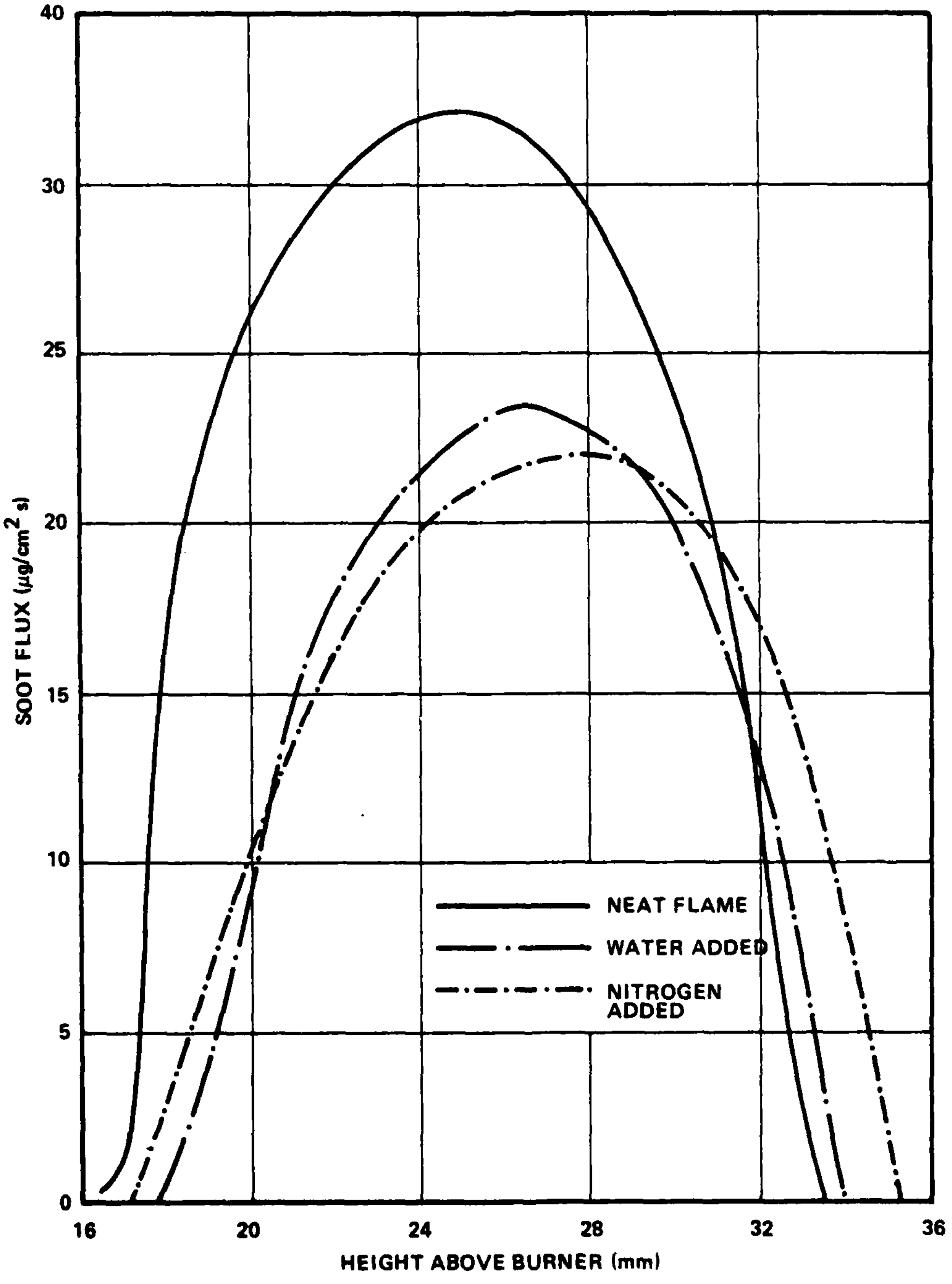


Figure 6. Soot Flux Profiles for the Three Ethylene Diffusion Flames Along Their Central Vertical Axes

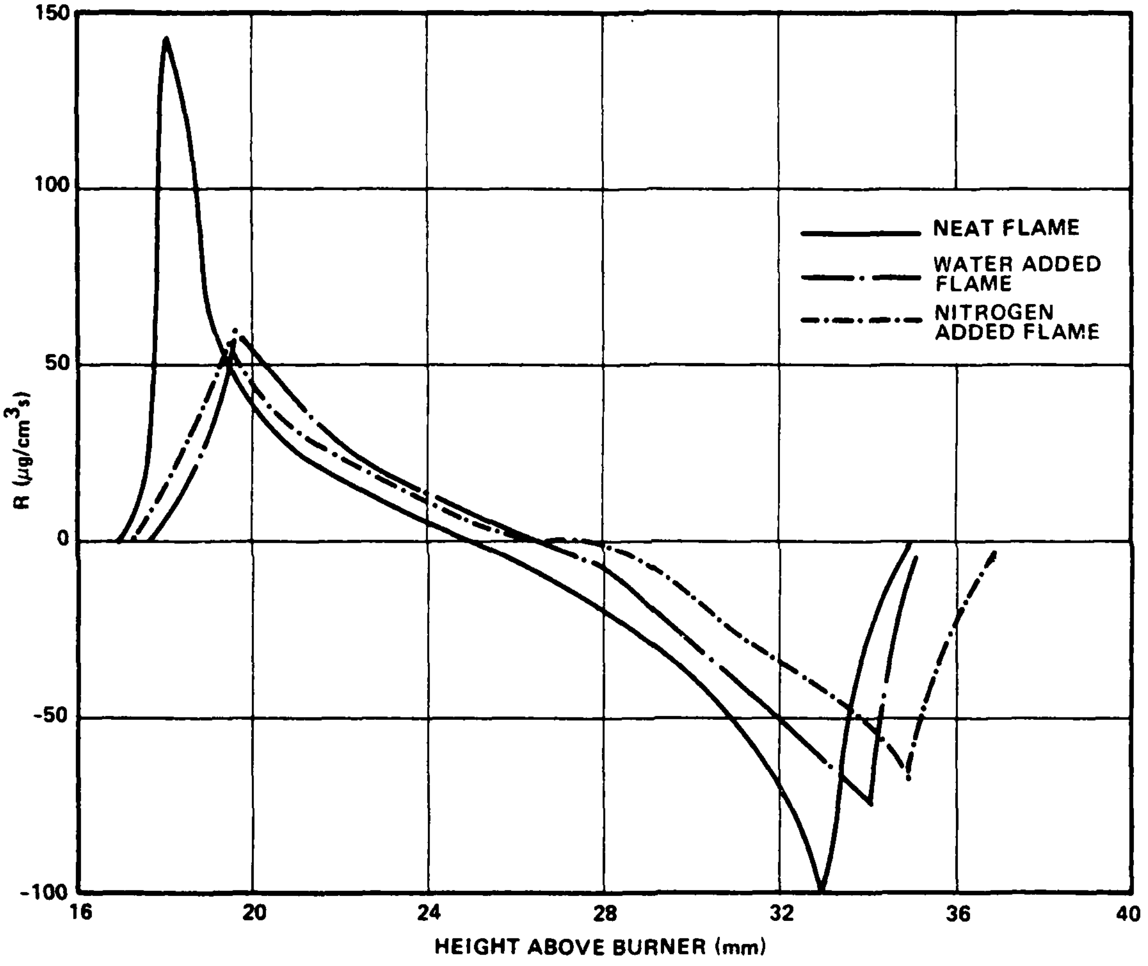


Figure 7. Comparison of Soot Formation/Oxidation Rate Profiles Along the Central Vertical Axes of Three Ethylene Flames

It is desirable to decouple the effects of formation and oxidation. This can be done by examining the part of the flame where soot formation has long since ceased and developing an expression for soot oxidation.

It is believed by many researchers (24,25) that the primary oxidizer of soot in all but very lean flames is OH rather than O_2, O or H_2O. The rate of oxidation of soot must be a function of OH concentration and surface area of soot available for oxidation:

$$R_{ox} = k[OH]\pi d^2 N \tag{19}$$

where R_{ox} is the rate of soot oxidation (which is the negative of the R defined as soot formation rate earlier), d is an average soot particle diameter and N is the number density of particles. Thus $\pi d^2 N$ represents the total surface area of soot. Surface areas can be represented in terms of known quantities such as soot concentration:

$$[soot] = N\rho\pi d^3/6 \tag{20}$$

where ρ is the density of an individual soot particle. Substituting for d^2 in equation (19):

$$R_{ox} = k \frac{[OH][Soot]}{d} \frac{6}{\rho} \approx k' \frac{[OH][Soot]}{d} \tag{21}$$

Incorporating an Arrhenius temperature dependence:

$$R_{ox} = \frac{[OH][Soot]}{d} A \exp [E_a/RT] \tag{22}$$

Plotting $\ln \left\{\frac{R_{ox}\, d}{[OH][Soot]}\right\}$ vs $\frac{1}{T}$ will yield a value of activation energy for soot oxidation.

In the above treatement, values for R_{ox}, [Soot], and T are available experimentally or calculated from experimental data, with d and [OH] to be determined. A paper by Fenimore and Jones (24) aids in estimating these values. They argue that an estimation of soot diameter during oxidation in diffusion flames can be obtained from a comparison between soot loss and CO loss. The relationship given by Fenimore and Jones (F&J) is:

$$\frac{d \log [Soot]}{d \log [CO]} \approx \frac{0.5 \times 10^{-6} (cm)}{d} \tag{23}$$

with the argument including the fact that the only important oxidant of both soot and CO is the OH radical, CO being oxidized by the reaction

$$CO + OH \rightarrow CO_2 + H \tag{24}$$

the rate expression for which has been found to be (24):

$$\frac{-d\,[CO]}{[CO]\,dt} = 4.16 \times 10^{11}\,[OH]\,\exp\left\{-\,1.08\ \text{kcal}/RT\right\}\quad \text{sec}^{-1} \tag{25}$$

Since the mass spectral study of the present program gives CO profiles, it is possible to obtain both d and [OH] respectively from equations (23) and (25).

Three processes occur simultaneously that determine the CO concentratior at any point in the flame: formation, oxidation and diffusion. If a point is chosen sufficiently high in the flame, CO formation is no longer occurring. Referring back to Figure 2, the species profiles for the neat flame, it can be seen that above about 24 mm, all hydrocarbons have been destroyed. Thus, it is impossible for CO to be formed above this point. Corrections for diffusion are made by considering the lowest part of the flame. Low in the center of the flame the temperature is too low for hydrocarbon oxidation to be important. The CO present there must have diffused in from the hotter surroundings of the flame where hydrocarbon oxidation to CO is possible. One can look at the CO profile in Figure 2 between say 6 and 14 mm above the burner and attribute the increasing CO concentration entirely to diffusion from the surroundings. This diffusion rate can be quantified by first assuming uniform concentration of total species into which CO is diffusing and then applying temperature corrections. For example, consider the interval between 9 and 10 mm above the burner. Concentrations of CO can be found for points 9 and 10 mm above the burner. Temperature corrections are then made and a net diffusion from the surroundings to the area between 9 and 10 mm above the burner can be calculated. When such an operation is performed at each point between 6 and 14 mm, an average increase in [CO] due to diffusion into the center of the flame per mm of height can be found. Going then to the upper part of the flame, [CO] is corrected for diffusion, with the resultant Δ[CO] being due solely to CO oxidation. This, combined with the decay in soot concentration in equation (25), allows the estimation of d. (It is assumed that soot does not diffuse radially in this system.) Values estimated for d as a function of height above the burner for the neat flame are plotted in Figure 8.

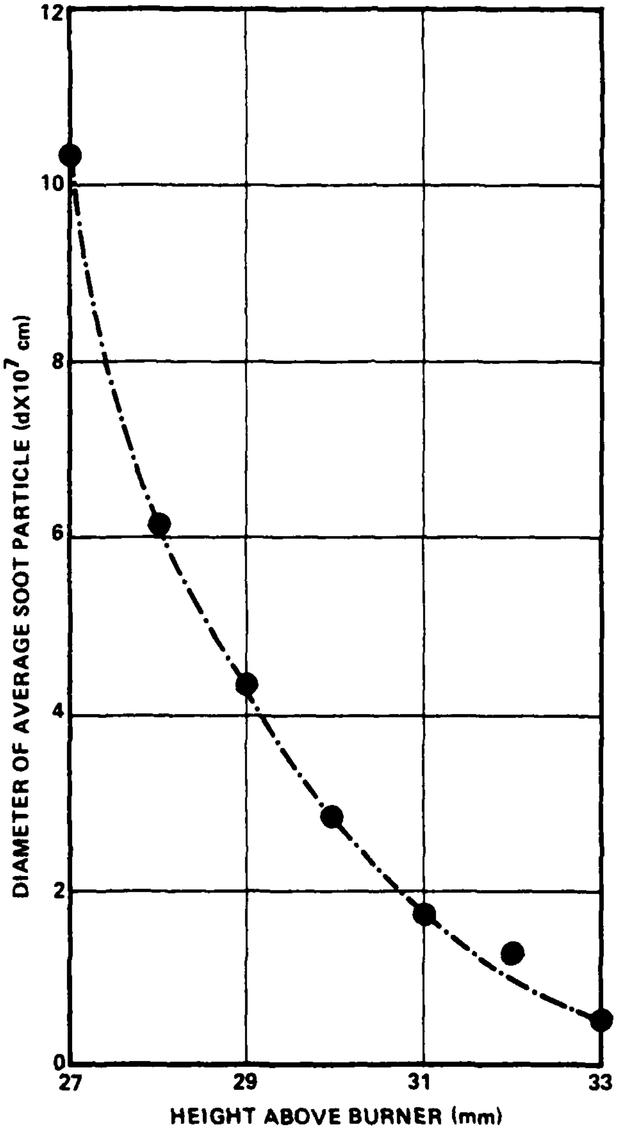


Figure 8. Estimates of Soot Particle Size Along the Central Vertical Axis During the Oxidation Process in the Neat Ethylene Diffusion Flame.

F&J (24) make several statements concerning the size of soot particles produced in small laboratory diffusion flames. Among these statements are: 1) soot particles grow rapidly to spheres of about 1×10^{-6} cm regardless of the nature of fuel, and then begin to aggregate, 2) aggregates larger than 5×10^{-6} cm are large enough to resist oxidation, and 3) a 20% oxidation of CO corresponds to a 40% drop in soot concentration, with the remaining soot having an average diameter of 2×10^{-7} cm. In the present work, a 40% reduction in soot concentration has occurred in the neat flame at about 31 mm above the burner, at which point soot average diameter is estimated as 1.8×10^{-7} cm. In addition, all soot produced in the present flames is oxidized before reaching the flame tip. It would seem then, that the findings here are consistent with those of F&J.

The concentration of OH can be calculated using the diffusion-corrected values for [CO] in equation (27). With all the parameters known, it is possible to plot $\ln \left\{ \frac{R_{ox}\, d}{[OH][Soot]} \right\}$ vs $\frac{1}{T}$. This plot is presented for the neat flame in Figure 9. It is interesting to note that quite a straight line can be drawn up to a point corresponding to 33 mm above the burner - or just below the point where all the soot is oxidized. At this point, the relationship seems to break down and the value for $\ln \left\{ \frac{R_{ox}\, d}{[OH][Soot]} \right\}$ is much higher. There can be two explanations, not mutually exclusive, for this phenomenon: 1) as [Soot] approaches zero the accuracy of measurement must decrease, and 2) according to Howard and co-workers (25), soot oxidation high in a flame can lead to rapid breakup of soot agglomerates, exposing fresh surface area, thus making calculated values for d too high.

Taking the slope of the straight line formed by the six other points in Figure 9, an activation energy of 6.9 kcal/mole is obtained. Several authors have reported activation energies for soot oxidation in various systems. In most cases, activation energies have been of the order of 40 kcal/mole, but the studies were based on the assumption that O_2, not OH, was the principal oxidizer. The now more accepted theory, however, is that OH is the main oxidation source except at very lean conditions, and it is this premise upon which the oxidation argument presented above is based. No value for the activation energy of the OH + soot reaction has been reported, although there are indications (24,25) that it is lower than that for O_2 + soot.

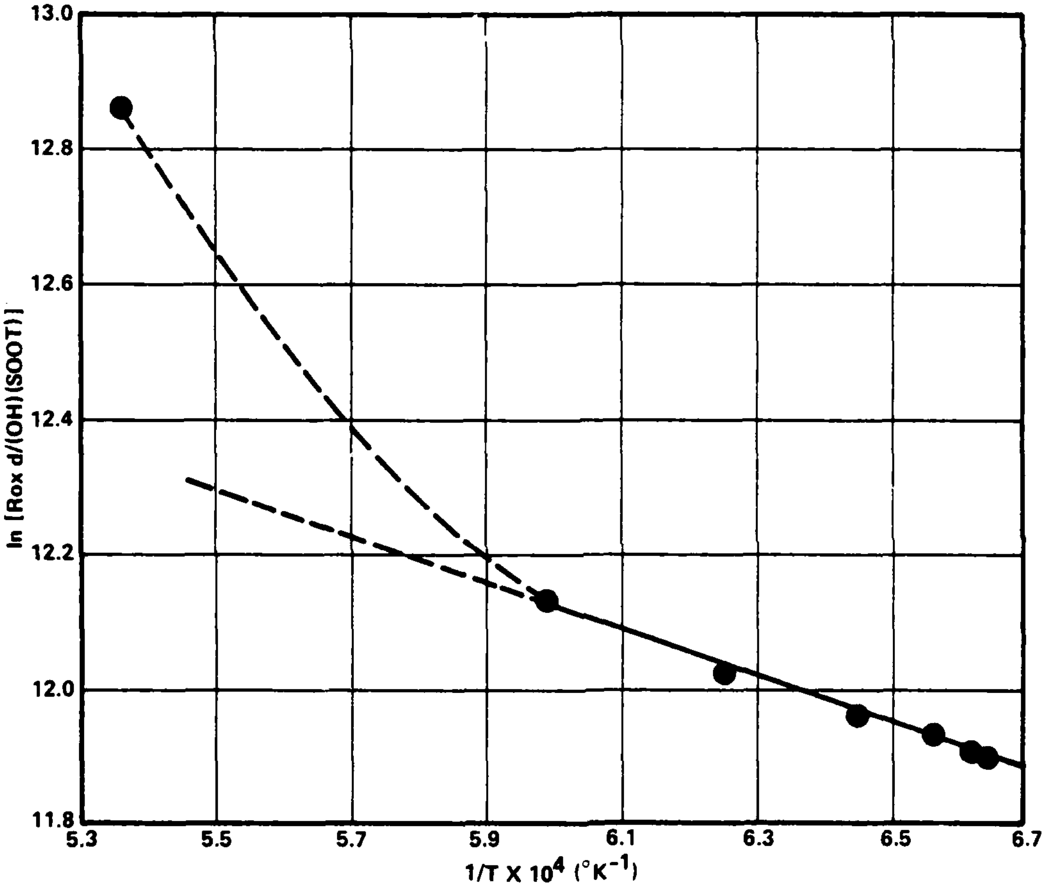


Figure 9. Determination of Activation Energy for Soot Oxidation in the Neat Ethylene Flame

Figures 10 and 11 depict the corresponding soot particle size estimate and Arrhenius relationship for the water-added ethylene diffusion flame. Particle size is compatible with the neat flame. Activation energy for the oxidation of soot by OH in the water-added flame is about 8.6 kcal/mole. There is considerable scatter in the data, and the activation energies found for the neat and water-added flames are within experimental error of one another.

The only apparent effect that the addition of water to ethylene has on soot formation is a thermal one. The flames are alike in most respects. The basic difference is a lower temperature in the lower part of the water-added flame with a corresponding reduction in soot. Both reductions are matched by virtually identical reductions in the nitrogen-added flame. In addition, there seems to be little difference in soot oxidation rates with and without added water.

The only chemical species that seem to be affected by water are the minor ones: 1,3 butadiene, vinyl acetylene and diacetylene. All three are reduced in the water-added flame, and all three are possible intermediates in the soot formation process. They are formed by various previously discussed addition and dehyrogenation reactions involving ethylene and acetylene. It does not seem likely that water reacts with any of these or with acetylene to reduce soot formation as no reaction products can be seen. It is more likely that the lower temperature in the lower part of the water-added flame slows the formation of the minor species. This in turn probably causes a reduction in soot formation, although it is possible that the two phenomena occur in parallel rather than one being causitive.

B. Benzene Diffusion Flames

Benzene was chosen for study because, not only do aromatics produce more soot than aliphatics, but the possibility exists for soot formation routes different than those for aliphatics which could be affected differently by added water.

A benzene diffusion flame can be established by igniting a mixture produced by bubbling argon through benzene. Such a flame can only be made about 1 cm high before soot breaks through the flame tip. This cannot be corrected merely by increasing the argon flow since this in turn increases the benzene flow. Instead, a secondary stream of argon, parallel to that bubbling through the benzene, was incorporated with two streams being mixed prior to entering the

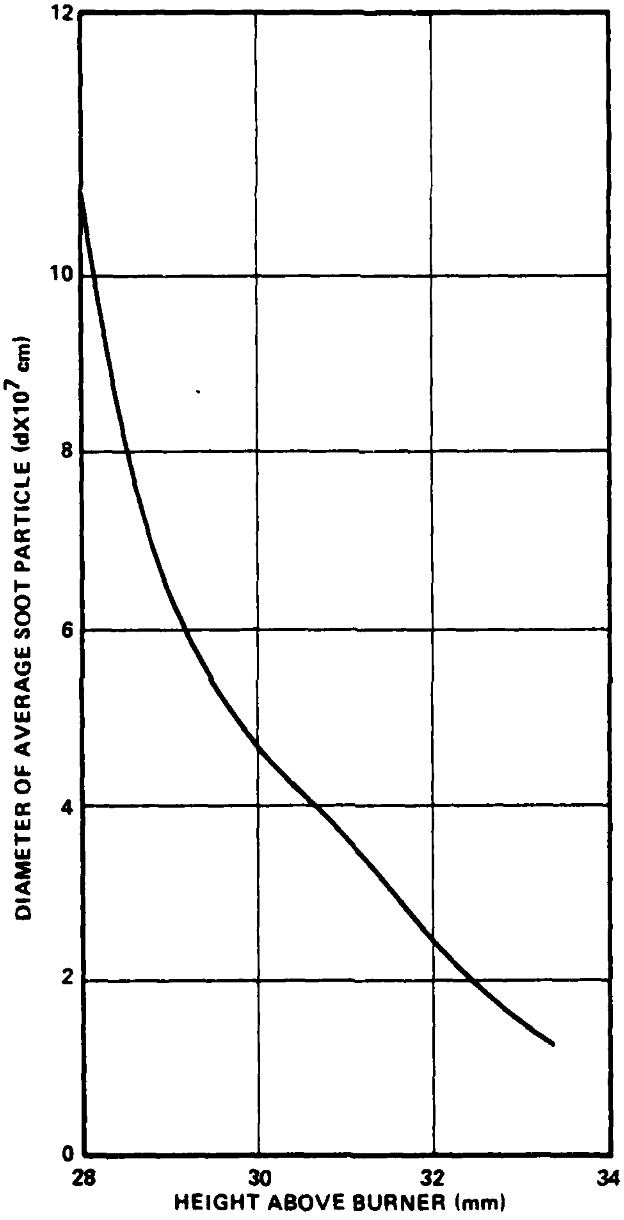


Figure 10. Estimates of Soot Particle Size Along the Central Vertical Axis During the Oxidation Process in the Water-Added Ethylene Diffusion Flame

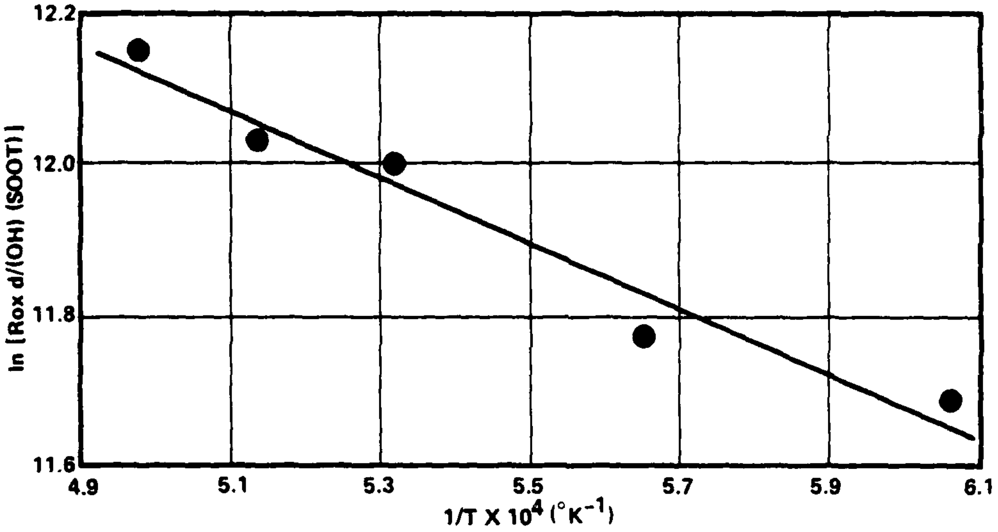


Figure 11. Determination of Activation Energy for Soot Oxidation in the Water-Added Ethylene Diffusion Flame

burner tube. This modification eliminates soot breakthrough but still results in a 1 cm high flame - too small for study. Consequently it was decided to add a non-sooting fuel, hydrogen, to the secondary argon stream. It is then possible to produce a flame 3.6 cm high (chosen as a convenience for comparison with ethylene) which produces a measurable but not excessive amount of soot. When water is needed, the argon/hydrogen mixture is routed through a heated water bath.

It is impossible in this system to study a "neat" benzene flame. Instead, a combination of 9.56×10^{-4} g/s benzene, 1.42×10^{-4} g/s hydrogen and 1.38×10^{-2} g/s argon was used as the "basic" flame. To obtain variations, different amounts of water or additional argon (refer to Table 1) were added. The variations used included addition of $.78 \times 10^{-4}$ g/s, 6.61×10^{-4} or 11.1×10^{-4} g/s of water (referred to as "low," "middle" and "high" water respectively), and an increase in argon to 1.90×10^{-2} g/s ("high argon"). Room temperature velocities for the mixtures are: 3.68, 3.77, 4.00, 4.21 and 4.81 cm/s respectively for the basic, low, middle, high water and high argon flames.

Temperature profiles for the basic, middle water, high water and high argon flames appear in Figure 12. The low water temperature profile virtually parallels the basic flame temperature profile and is omitted to lessen the complexity of the figure. The similarity in temperature between the basic and low water flame is to be expected when one considers that the water makes up only 1.2% by weight (0.02 mole fraction) of the composition of the low water flame.

The entire series of benzene flames are cooler than their ethylene counterparts. This is to be expected as, first of all, there is substantially more diluent in all the benzene flames, thereby explaining the lower temperatures in the lower part of the flame, and second of all, the adiabatic flame temperature for benzene is lower.

The heat needed to raise the temperature of argon is constant at 4.97 cal/deg mole, while that for water increases from 8.28 cal/deg mole at 398°K to 11.24 cal/deg mole at 1600°K (18). The high water flame contains a flow of 6.2×10^{-5} mole/s of water, which is replaced by 13.1×10^{-5} mole/s of argon in the high argon flame. The two flames should exhibit the same temperature (at least low in the flame) when the relative heat sink effect of the additives is equal. The calculated point where the temperatures would be exactly equal is 1290°K. At 18 mm above the burner, however, where the high argon flame is

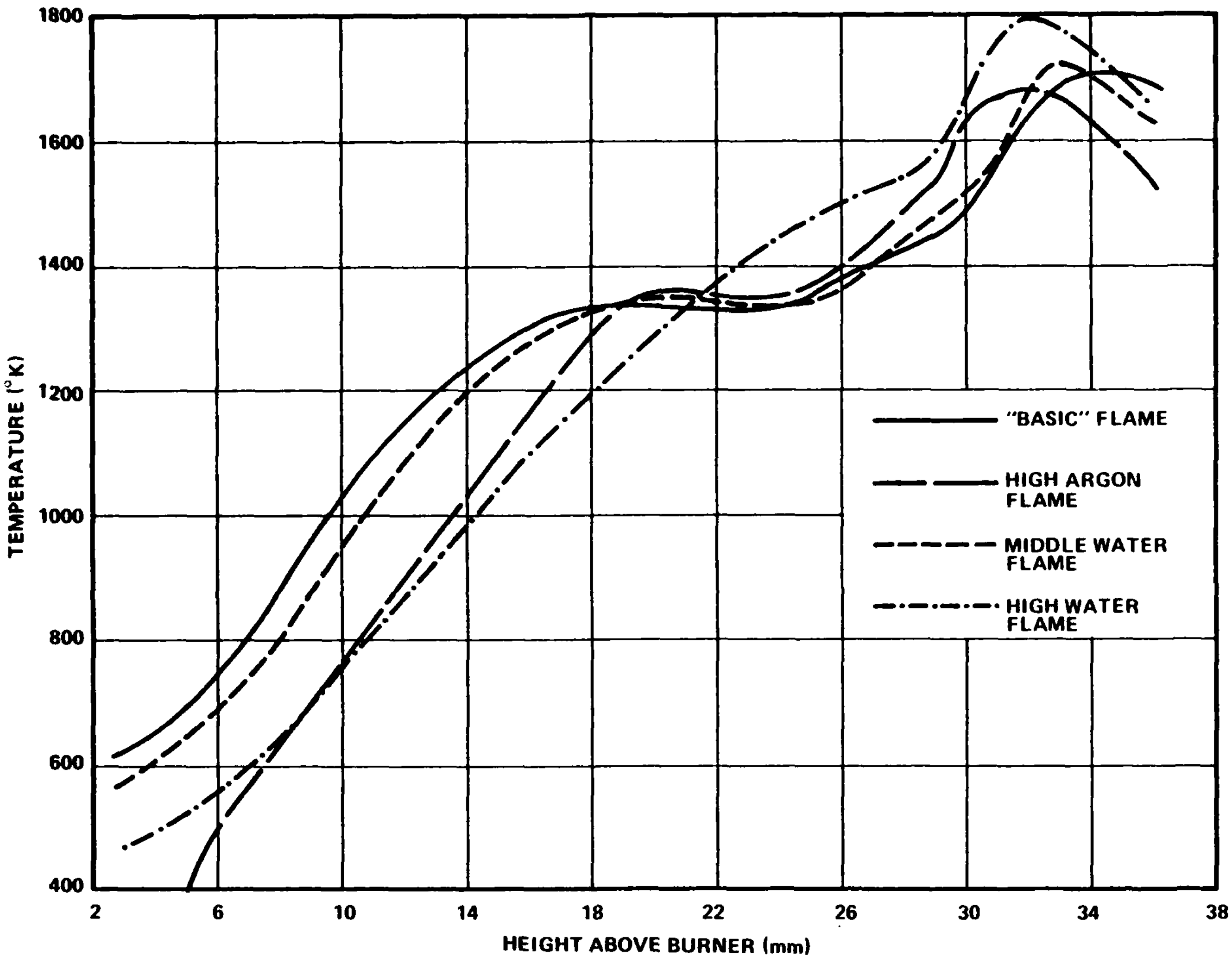


Figure 12. Temperature Profiles for Benzene Flames - Central Vertical Axis

about 1290°K, the high water flame is only 1200°K, or 90°K lower than it should be. This is probably outside the limits of experimental error, and indicates inhibition of an exothermic reaction.

Mass spectrographic species profiles for benzene flames are more difficult to decipher than those for ethylene flames because of fragmentation of benzene itself. Nevertheless, concentration profiles for the major species present in the basic and high water flames have been extracted from the data. The basic flame profiles are depicted in Figure 13. Comparing these profiles to those for the ethylene flames, two differences are immediately obvious: the lack of rapid fuel (benzene) depletion low in the flame, and the corresponding lack of argon increase. Both of these results are, of course, due to the fact that the argon which is premixed with the fuel is in greater concentration than argon diffusing in from the annular region, so that the net effect is actually a slight outward diffusion of argon - at least after the first few millimeters. The lack of a large argon concentration gradient in turn prevents benzene from exhibiting the large concentration gradient that was seen for the fuel in the low parts of the ethylene flame. Hydrogen diffusion is about six times as rapid as benzene, which accounts for its depletion low in the flame. Species profiles for the high water flame, not reproduced here, exhibit more scatter but are essentially identical to the basic flame profiles (with the exception, of course, of increased water).

A reaction product of benzene pyrolysis is acetylene, although its concentration never rises above 0.5 mole percent. The minor intermediates observed in the ethylene flames are not seen here, but would be masked by benzene. Nothing is observed that could be construed as resulting from a chemical reaction involving water. No aromatic species other than benzene itself are observed. It would seem then, at least to the limits of the instrumentation, that benzene behaves similarly to ethylene, breaking down to form acetylene and then presumably building to form soot from the acetylene base.

Soot flux gradients at varying heights 5 mm apart are shown in Figure 14 for the basic benzene flame. These assume the same characteristic shapes as found with ethylene and discussed in the previous report. Soot flux profiles along the central vertical axis for the basic, high argon and low, middle and high water flames appear in Figure 15. The temperature dependence of the soot formation process can be qualitatively seen. The more water or argon in the

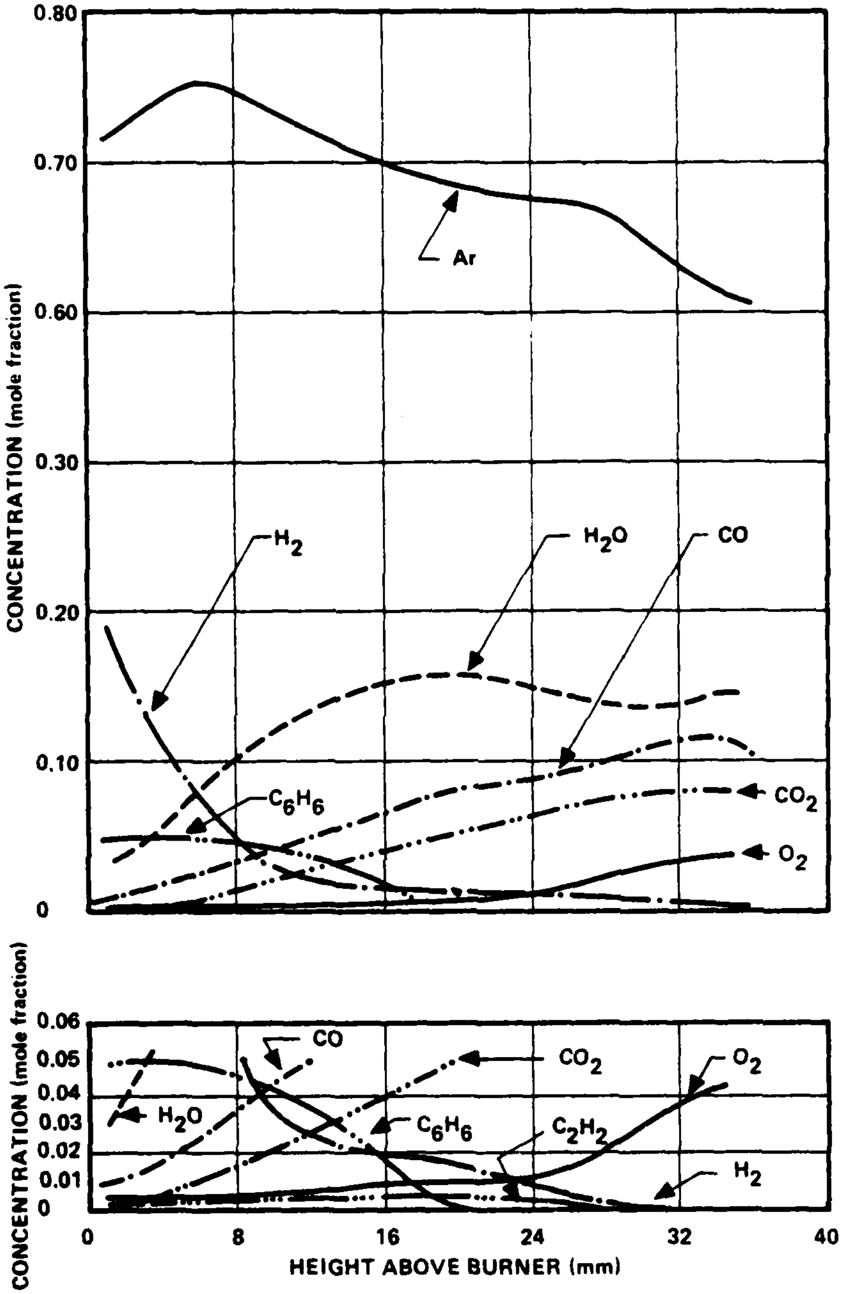


Figure 13. Mole Fractions of Major Species in the "Basic" Benzene Flame - Central Vertical Axis

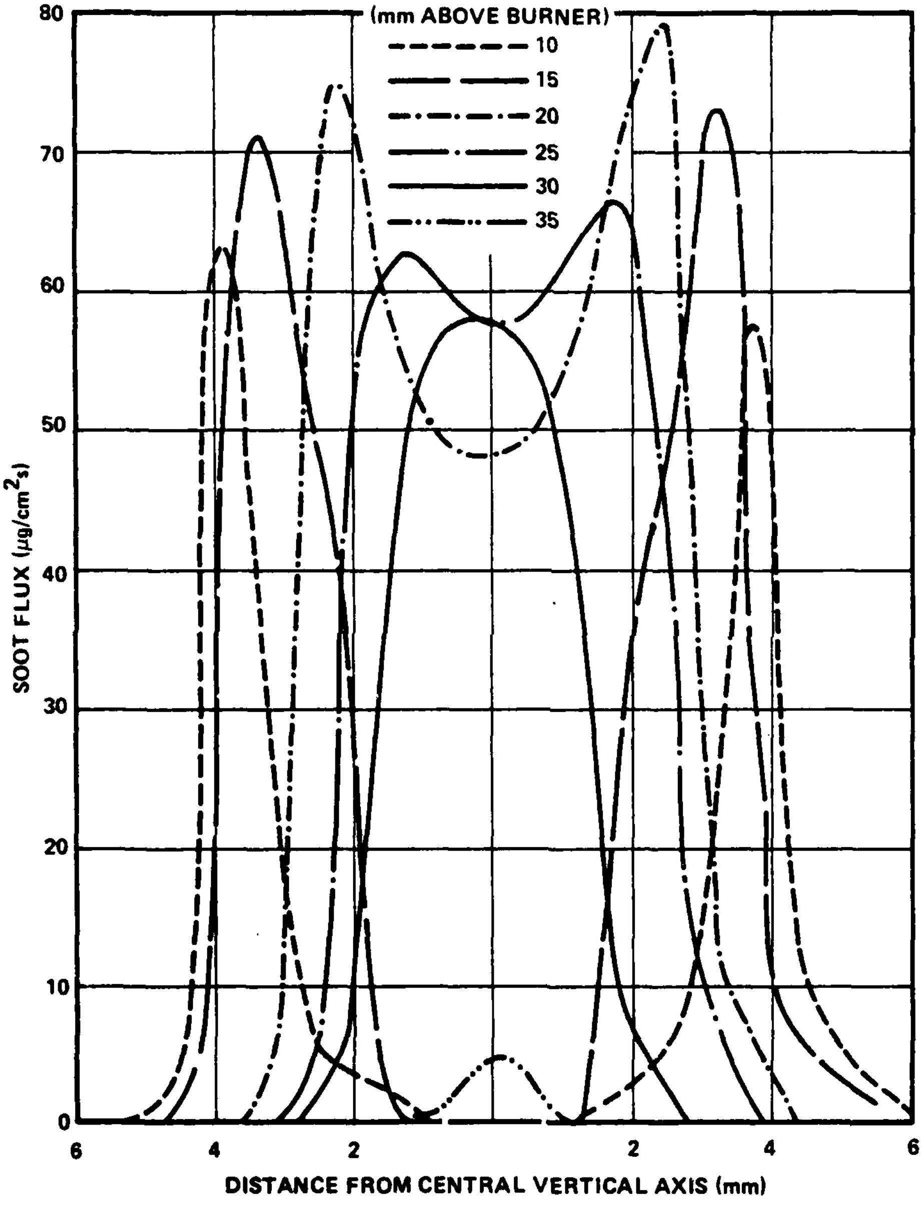


Figure 14. Soot Flux Profiles at Various Heights Above Burner for the Basic Benzene Flame

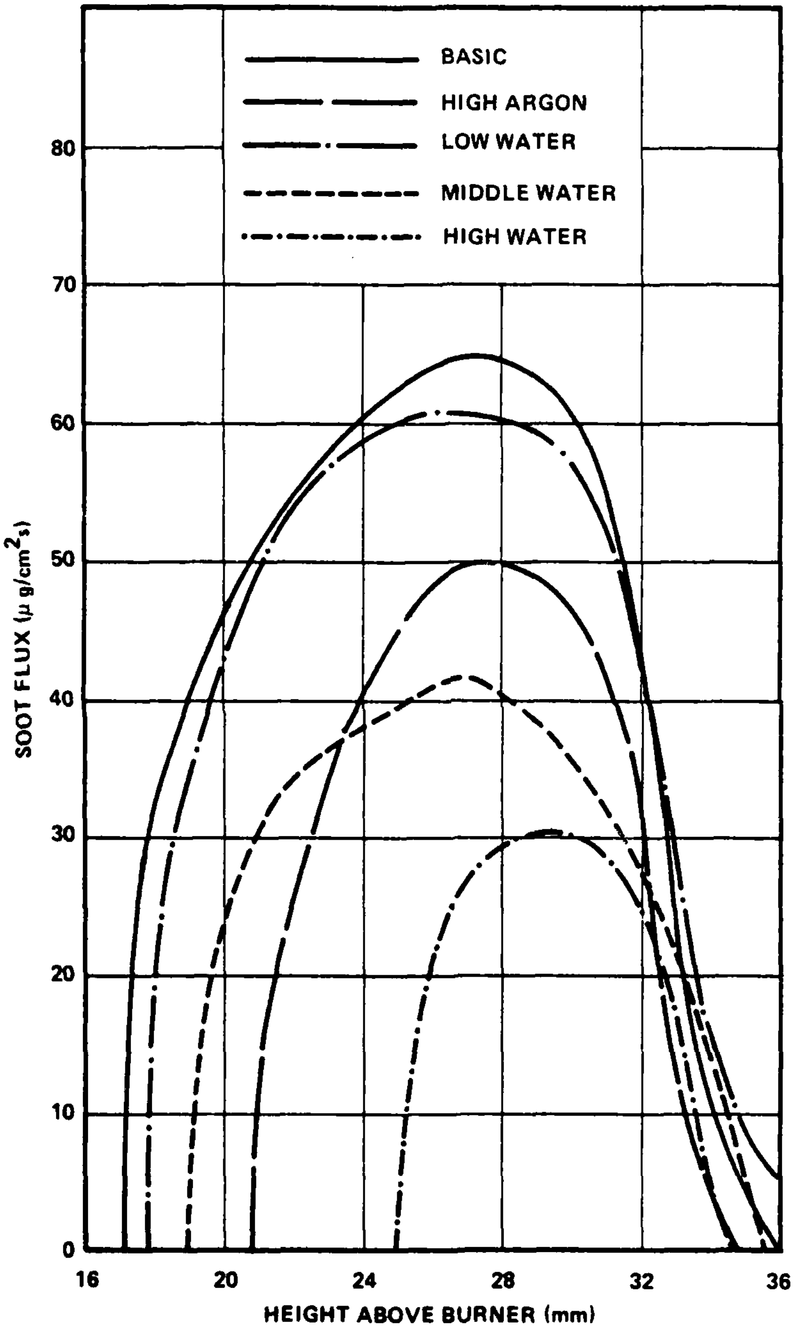


Figure 15. Soot Flux Profiles Along Central Vertical Axis for Benzene Flames

flame the longer it takes to reach a temperature where sooting can begin. Soot oxidation in the upper part of the flames, however, follows more or less the same pattern for all conditions, which is similar to the scheme of the ethylene flames but decidedly more pronounced with benzene. This is most likely because the hydrocarbon/additive ratio is much smaller in the benzene flames than in the ethylene flames. Soot formation rate curves for all but the low water flame are shown in Figure 16. The low water flame virtually duplicates the basic flame as would be expected from the similarities in both soot and temperature profiles.

The basic differences in the formation rate curves are in the height and position of the highest soot formation rates achieved. Roughly speaking, the more water present, the higher in the flame the onset of sooting occurs and the smaller is the maximum soot formation rate. Sooting onset definitely appears to be temperature dependent with a temperature greater than 1300°K needed for sooting to occur. The more diluent added, the longer it takes to reach this point, and the later the onset of sooting.

Overall soot reduction with water addition is also partially due to a temperature effect, but this does not seem to be the only factor. Comparing the basic and the high argon flames of Figure 16: In the dark zone, temperatures of the high argon flame lag behind those of the basic flame by about a distance of 4 mm (e.g., the basic flame reaches 1000°K at about 9.5 mm above the burner, and the high argon flame reaches 1000°K at about 13.5 mm above the burner). Correspondingly, soot onset of the high argon flame occurs 4 mm higher than that of the basic flame. The water-added flames do not follow this relationship. For instance, the high water flame lags only about 1 mm behind the high argon flame in temperature, but does not reach soot onset until a full 4 mm higher than the high argon flame. This would seem to indicate that something other than thermal effects is aiding in soot reduction.

The above statement is augmented by the fact that the high argon and high water flames should exhibit roughly the same heat-sink effect. Yet, the maximum soot formation rate is reduced nearly twice as much in the high water flame as in the high argon flame when compared with the basic flame. However, no corresponding results in the mass spectrometer chemical species profiles were observed.

The soot reduction question, however, can be approached in an additional way. As has been previously mentioned, all flames when probed for soot were

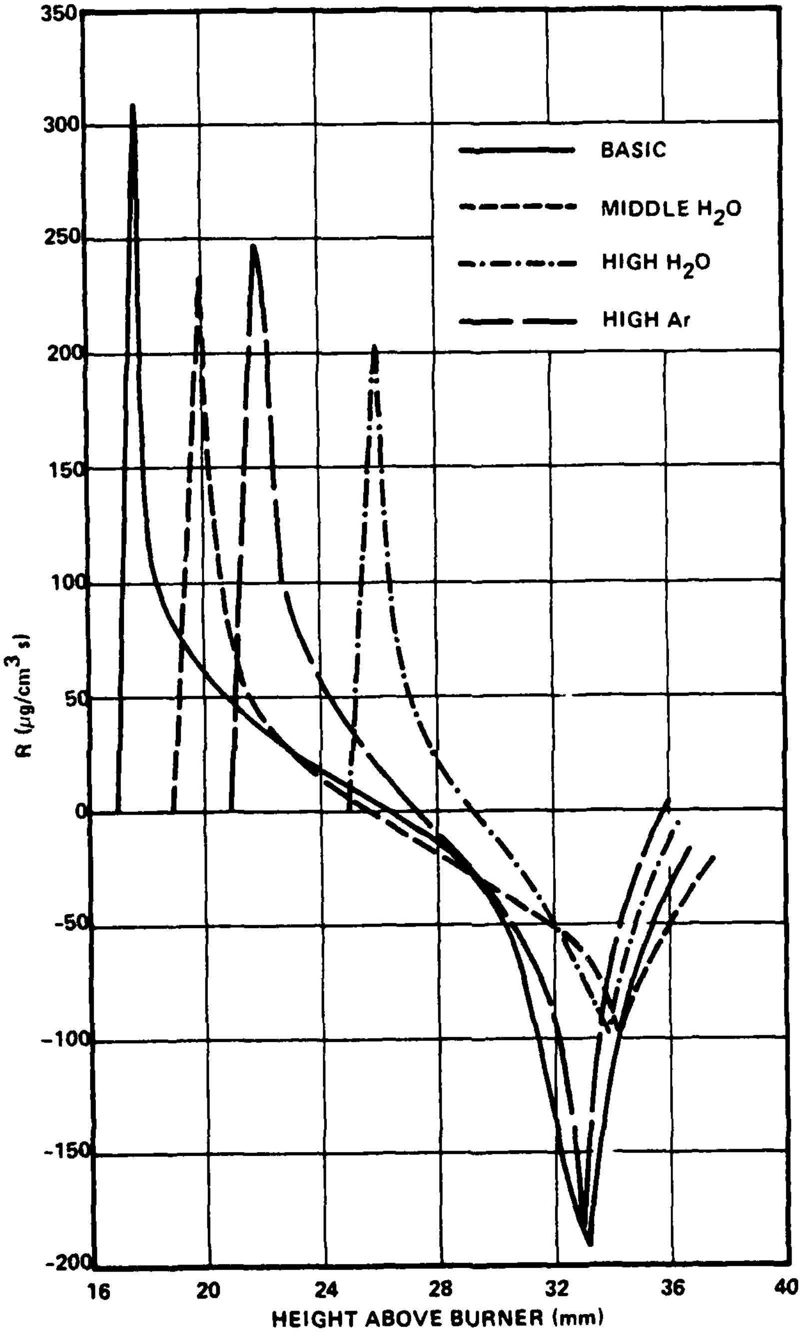


Figure 16. Comparison of Soot Formation/Oxidation Rate Profiles Along the Central Vertical Axes of Four Benzene Flames

found to have a deposit of a tar-like substance present at positions just below the onset of soot formation. Although it was not possible to duplicate the soot flux-optical density calibration process (16) for tar because of its limited concentration, it is possible to compare tar profiles among themselves using artificially that calibration scale of optical density attained per unit time of the probe in the flame. Such profiles are shown for the five benzene flames along the central vertical axis in Figure 17.

In general, tar begins to form about 6 mm below the onset of sooting. Tar concentration increases gradually at first, and then rapidly up to a maximum. The tar concentration maximum corresponds closely to the position of sooting onset and above this maximum drops sharply to zero.

Tar concentration seems to be dependent on both temperature and water concentration. Looking at the two water-free flames of Figure 17, where the effect can only be thermal, the cooler high argon flame produces less tar than does the basic flame. The addition of water, however, causes an increase in tar concentration, an effect that is tempered by the accompanying lower temperatures of the water-added flames (with the high water). This then is a piece of evidence that water is interacting with flame species in other than a purely thermal way.

It is unknown if tar is being formed separately from soot or if the two processes are related. The amount of tar formed is very small, and as mentioned before, no change in detectable chemical species upon addition of water can be observed. On the other hand, tar and soot seem to be linked through the correlation between tar maximum and soot onset. There is also a report by Prado and Lahaye (8) in which considerable tarry matter was seen to form prior to soot in thermal decomposition experiments. The tar concentration went through a maximum near the point of soot onset.

An attempt was made to characterize the tar produced in the benzene flames. This was done by first collecting the tar on a continuously moving ribbon passing through the tar-producing region of the flame. The collected tar was wiped off the ribbon into a tube containing chloroform where it was dissolved. The solvent was then evaporated and the tar studied with a Nicolet Fourier Transform Infrared Spectrophotometer, a spectrum from which is shown in Figure 18.

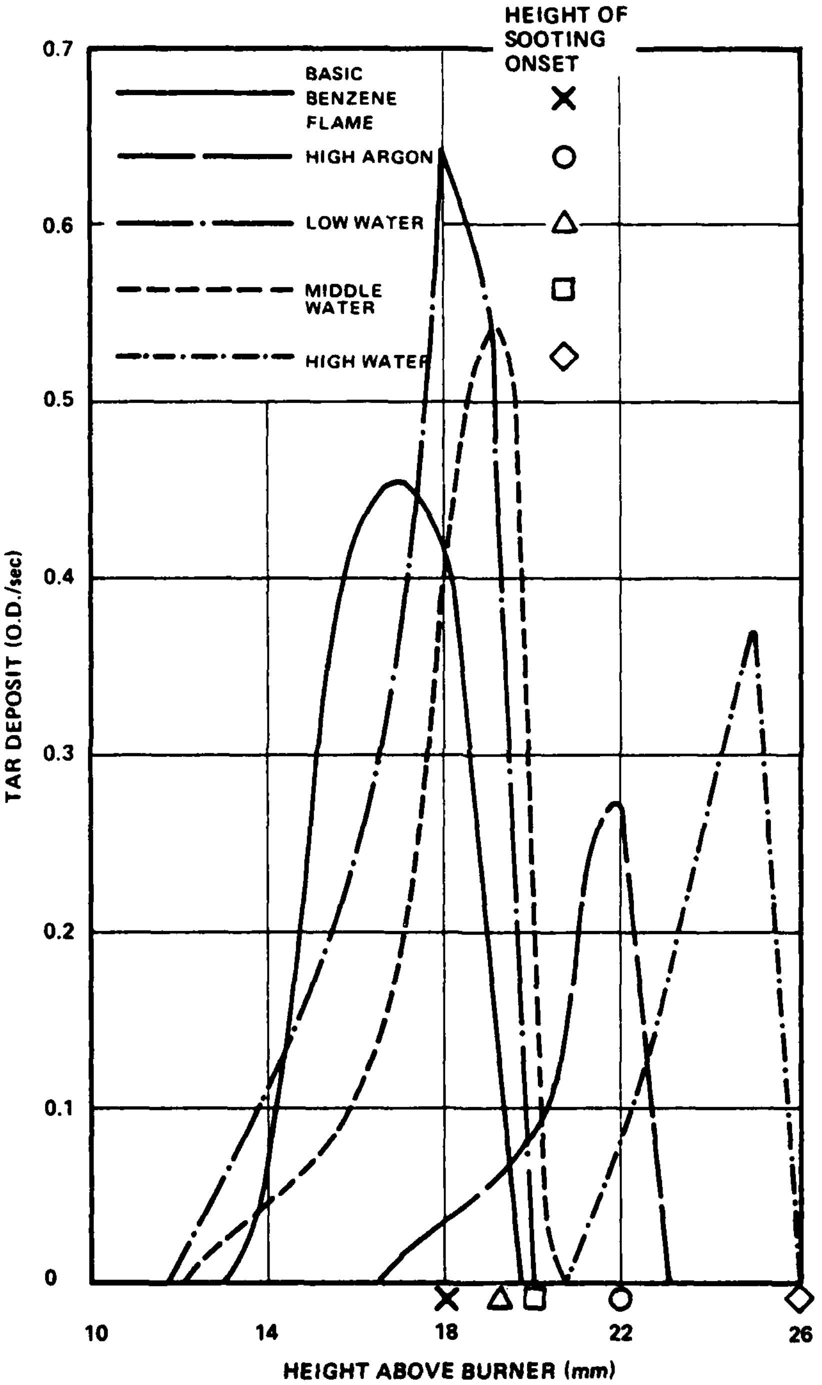


Figure 17. Relative Tar Profiles of Benzene Diffusion Flames - Central Vertical Axes (Position of Soot Onset is Also Shown)

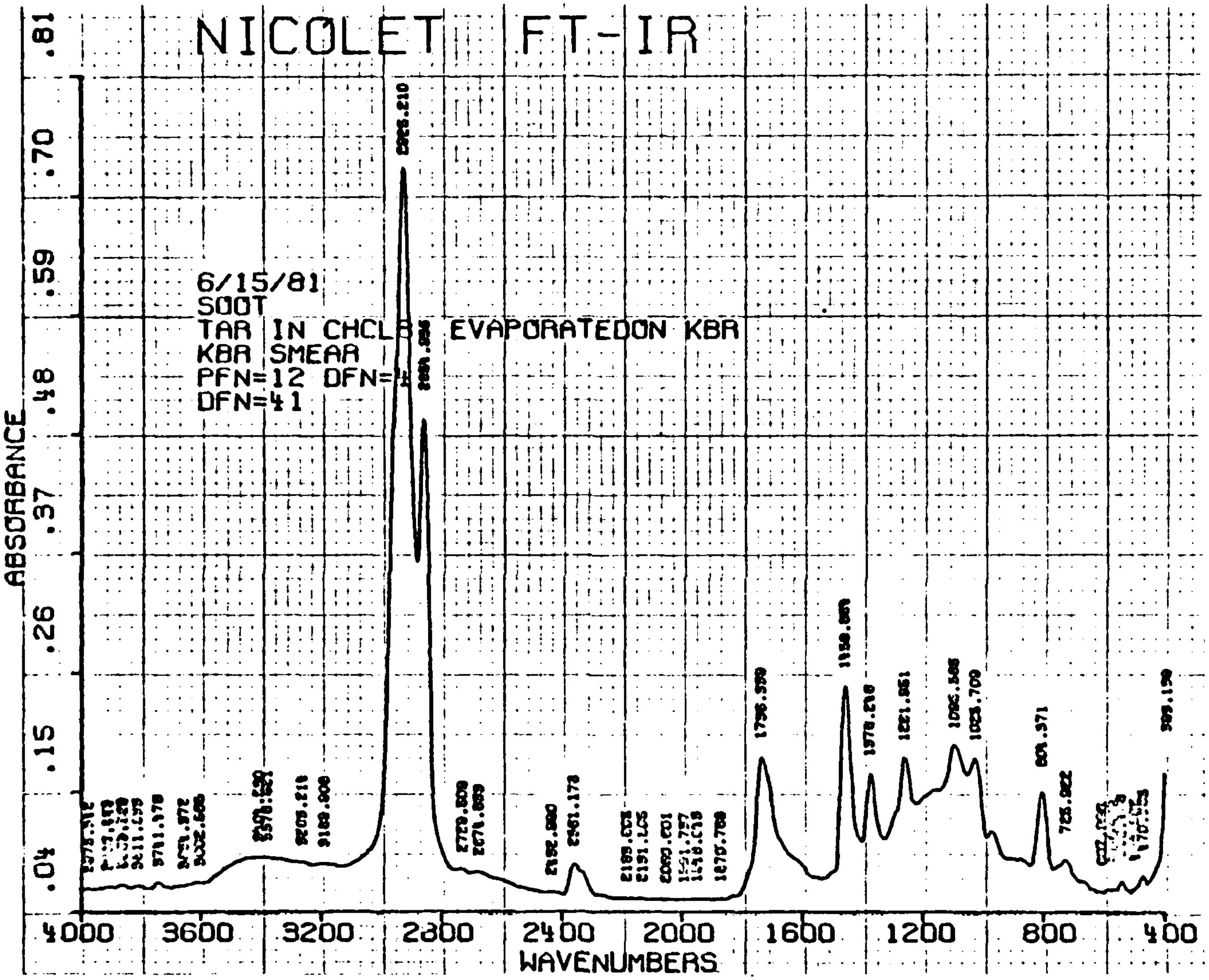


Figure 18. FTIR Spectrum of Tar in a Benzene Diffusion Flame

The spectrum is complex, and more than one species could be present. In fact, the material may not even possess a defined molecular structure. There is no evidence of aromatic rings. The large doublet near 2900 cm^{-1} is indicative of C-H stretching, and correspondingly the peak near 1400 cm^{-1} represents C-H bending, neither of which band is definitive. The peak near 1750 cm^{-1} is representative of carbonyl stretching, possibly more than one kind of carbonyl, and the weak, broad band between 3200-3500 cm^{-1} could be indicative of OH. The peak near 2400 cm^{-1} is residual chloroform solvent.

It was not possible within the scope of the study to pursue the subject of tar formation and its relationship, if there is one, to soot. The foregoing data represent an initial approach to what might be a fruitful research area.

CONCLUSIONS

1) The effect of water addition on soot formation may depend on the fuel involved. With ethylene, soot reduction achieved by water addition is matched by a similar soot reduction achieved by adding a thermally equivalent amount of an inert additive. With benzene, the soot reduction with water cannot entirely be explained thermally. Water causes a greater reduction in soot than does a thermally equivalent inert substance. This effect, however, is not accompanied by noticeable differences in the mass spectrographic profiles of the chemical species, although the effect may be below the sensitivity of the present system. There is supporting evidence, however, in the fact that oxygen-containing tarry substances observed prior to soot formation increase in concentration with increasing water addition. This effect is moderated and can be reversed by the accompanying lower temperatures.

2) Decomposition of both ethylene and benzene involves the formation of acetylene as a reaction intermediate. With the ethylene system (and conceivably with benzene also) unsaturated species such as 1,3 butadiene, diacetylene and vinyl acetylene are observed. These could be reaction products of acetylene and/or ethylene along the route to soot formation. Water addition results in a marked decrease in the concentrations of these three species, and the reason is most likely thermal. Corresponding changes in acetylene concentration were unobserved but would be expected to be very small.

3) Soot formation occurs mainly in a 1-2 mm vertical distance at the top of the dark zone, as seen by the very steep rise in soot formation rate at the onset of sooting.

4) Oxidation of soot by the OH radical occurs with an activation energy of about 7-8 kcal/mole. The presence of water does not affect the oxidation rate.

5) Calculated soot particle diameters in the upper part of the flames are compatible with results reported by Fenimore and Jones (24). At the point where soot formation is no longer important (about 27-28 mm above the burner rim in the ethylene systems), soot particle diameters are calculated to be of the order of $1\text{-}2 \times 10^{-6}$ cm. (F&J state that a particle of the order of 5×10^{-6} cm will survive oxidation in a laboratory diffusion flame.)

6) The phenomenon of oxygen being present in the center of a diffusion flame, first reported in the final report for the previous program (1), is confirmed. Oxygen evidently diffuses in around the burner rim, and is present at concentrations of about one-half mole percent low in the flame, increasing with flame height to a value of 2-3 mole percent in the higher parts of the flame.

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The continuation of an experimental flame study concerning the nonphysical processes that lead to soot suppression when water is added to fuel, begun in a previous program, is reported. The study included a mapping of temperature, chemical species and soot profiles of laminar diffusion flames with and without water added. Fuels studied included ethylene and a benzene/hydrogen mixture. Flames with nonreactive gases added (argon, nitrogen) were also studied for comparison purposes.

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20. ABSTRACT (continued)

The study concludes that the reduction of soot by water in an ethylene diffusion flame can be completely explained by thermal effects. The results are not as definitive for benzene. The addition of water causes a greater reduction in soot than does a thermally equivalent addition of argon, but no noticeable differences in chemical species profiles are observed. There is evidence, however, that water addition causes an increase in concentration of an oxygen-containing tarry substance present in the flame prior to soot formation.

During the course of the study it was also possible to estimate both soot particle diameters (1-2 x 10^{-6} cm at the beginning of the oxidation zone) and an activation energy for soot oxidation by the OH radical (7-8 kcal/mole). In addition, it was possible to confirm the presence of and quantify the oxygen concentration in the center of diffusion flames, first reported under the previous program.

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