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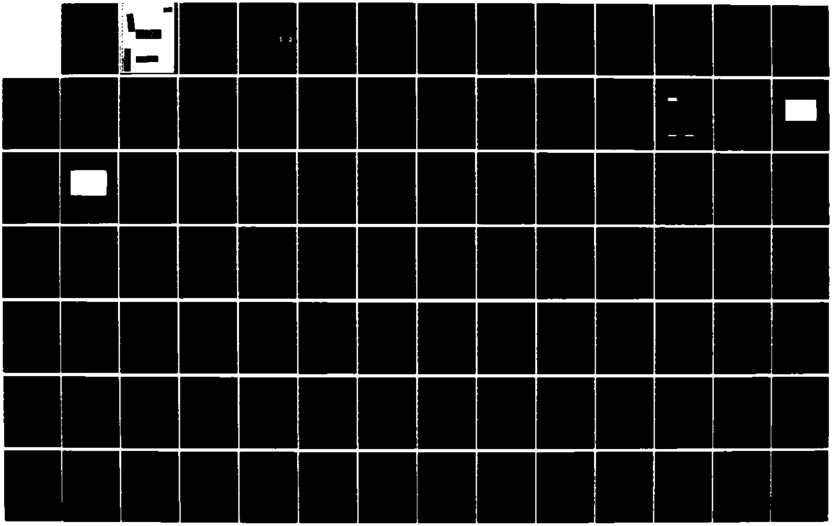

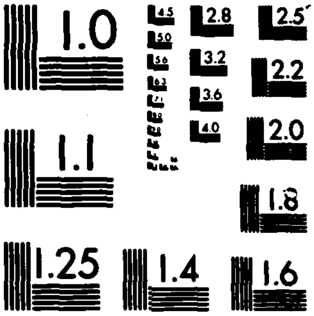
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MECHANISMS OF COMBUSTION OF HYDROCARBON/ALCOHOL FUEL BLENDS

FINAL REPORT

by

Dr. K. Seshadri

and

Dr. A. P. Hamins

December 1985

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Part 2

Part 3

Scientific personnel who participated in the project were:

1. Dr. Kalyanasundaram Seshadri, Assistant Professor of Chemical Engineering.
2. Dr. Anthony Peter Hamins. The research reported here is Mr. Hamins's PhD thesis. Mr. Hamins successfully defended his thesis on November 21, 1985.
3. Mr. Hareesh Thridandam.

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1. Hamins, A. and Seshadri, K., "Prediction of overall chemical kinetic rate parameters near extinction for diffusion flames burning multicomponent fuels," Combustion Science and Technology 38, 89-104, 1984.
2. Hamins, A. and Seshadri, K., "Structure of counterflow diffusion flames burning multicomponent fuels," Twentieth Symposium (International) on Combustion, The Combustion Institute, 1905-1913, 1984.
3. Hamins, A., Thridandam, H. and Seshadri, K., "Structure and extinction of a counterflow partially premixed diffusion flame," Chemical Engineering Science 40, No. 1, 2027-2038, 1985.
4. Hamins, A. and Seshadri, K., "The influence of alcohols on the combustion of hydrocarbon fuels in diffusion flames," to appear in Combustion and Flame, 1985.
5. Hamins, A., Gordon, A. S., Saito, K. and Seshadri, K., "Acetone impurity in acetylene from tanks," to appear in Combustion Science and Technology.
6. Hamins, A. and Seshadri, K., "The structure of diffusion flames burning pure, binary and ternary solutions of methanol, heptane and toluene," in preparation.
7. Hamins, A., Gordon, A. S., Saito, K. and Seshadri, K., "The structure of coflowing laminar diffusion flames burning diluted ethane, diluted ethylene and diluted acetylene in air," in preparation.

ABSTRACT

The results reported here directly supports the U. S. Army's research and development program in alternative fuels. Liquid fuels which are homogeneous solutions of hydrocarbon and alcohol fuels are considered here. Since combustion of diesel fuel resembles that in a diffusion flame, and because turbulent nonpremixed combustion can be considered as a statistical collection of strained, laminar flamelets, studies were performed on the structure and mechanisms of extinction of strained, laminar diffusion flames and strained laminar partially premixed diffusion flames. Use of alternate fuels often results in soot formation which causes easy detection of the vehicle. Therefore, studies were also performed to clarify the chemical mechanisms of soot formation in diffusion flames.

For a well controlled laboratory experiment it is essential that the composition of the fuel be known. Petroleum based fuels are often a blend of aromatics and aliphatic fuels. Therefore experiments were performed on representative fuels namely homogeneous solutions of heptane, toluene and methanol. Results were analyzed by use of asymptotic theories.

The experimental apparatus is described in Chapter II. Results of the research are discussed in Chapters III - IX. Each chapter has a brief abstract describing the results.

CHAPTER I

INTRODUCTION

The objective of this research was to support the U. S. Army research and development program in alternative fuels. A summary of the U. S. Army's alternative fuels program has been outlined by LePera (1984). It was shown that the program includes characterization of combustion of fuel blends (LePera 1982, 1984). The objectives of the U. S. Army's research program in this area was to develop needed technologies to enable greater use of commercially available alternative, or variable quality fuels (including fuel blends) in Army equipment without affecting their mission requirements, and to develop technology for utilization of variable quality fuels. The research discussed here directly addresses these questions, and are useful for evaluating the performance of fuel blends in military vehicles.

In practice liquid fuel is sprayed into the combustion chamber containing the oxidizer. Nonpremixed and partially premixed combustion of the fuel occurs in the chamber. Therefore fundamental studies on nonpremixed (diffusion) flames with fuel blends are relevant. The results of this research are particularly applicable to diesel fuels because combustion is characterized by diffusion of fuel through air such as that which occurs in a diffusion flame [LePera, 1982]. In addition, fundamental studies on the structure and mechanisms of extinction of diffusion flames give useful information related to fire safety (Williams, 1981). Therefore, the research reported here supports current research in U. S. Army laboratories aimed at reducing fuel fire threat associated with armored/tactical equipment. A problem associated with operation of military equipment with alternative fuel is soot formation which can lead to detection of the vehicle. In this research we also attempt to clarify mechanisms of soot formation in laminar flames.

The flow field in combustion chambers are often turbulent. There is convincing evidence that turbulent nonpremixed combustion can be modelled as an ensemble of laminar diffusion flamelets (Klimov 1963, Williams 1975, Peters 1984b) and laminar partially premixed diffusion flamelets (Peters 1984a, Seshadri *et al.* 1985). Klimov (1963) and Williams (1975) have clearly shown that the strain rate is a key factor affecting the structure of laminar flamelets in a turbulent flow. In the analysis of turbulent combustion the Kolmogorov length scale η, the Taylor length scale λ, and the integral scale l appear. Klimov (1963) and Williams (1975) show that in turbulent combustion, if the flame thickness δ satisfies the inequality $\eta < \delta < \lambda < l$ (which is generally the case in practice) then a laminar flame can exist in a turbulent flow. This laminar flame will be subjected to various rates of strain depending on the turbulent flow field in the combustor. In this report we have generated results for structure of nonpremixed, and partially premixed, laminar flamelets subjected to various rates of strain, and thus the results are useful in the analysis of turbulent combustion in engines.

Petroleum based fuels are a blend of aromatics, olefins, and saturates. The concentration of these components in the blend would depend on the fuel and its grade. For a well controlled laboratory study it is essential that the concentration of each of the components of the fuel blend be known. Therefore, we have used representative fuel blends such as homogeneous solutions of heptane/toluene and heptane/toluene/methanol, in known proportions. The mechanism of combustion of these blends are compared with the mechanisms of combustion of heptane, toluene, and methanol. The experimental configuration is the diffusion flame produced by directing an oxidizing gas stream downward onto the burning surface of a liquid fuel. It is often preferable to operate engines with excess air, because they result in lower smoke emissions. Therefore our studies on the structure and kinetics of diffusion flames and partially premixed diffusion flames were performed at conditions close to flame extinction. Studies on chemical mechanisms of soot formation in diffusion flames were performed in a coflowing diffusion flame because one can obtain a larger residence time in this configuration. The research is both experimental and theoretical.

1. EXPERIMENTAL APPROACH

To facilitate theoretical interpretation of experimental results it is essential to choose the proper experimental configuration. The counterflow configuration (Seshadri and Williams 1978, Tsuji, 1982) and the classical coflowing configuration (Burke and Schumann, 1928, Mitchell *et al.*, 1980, Glassman and Yaccarino, 1981) are the two principal approaches for studying the structure of laminar diffusion flames. An example of a diffusion flame in the coflowing configuration is the flame stabilized between fuel issuing from an inner tube and an oxidizing gas issuing from an outer concentric tube. Both, the fuel and oxidizer streams flow in the same direction. The resulting reaction zone has the appearance of a candle flame. A shear layer is produced and mixing of fuel and oxidizer occurs across this layer. In coflowing systems residence times and observation volumes are typically large. The convective flow toward the reaction zone is small, consequently buoyancy effects can be significant. In addition, one observes that fuel and oxidizer premix near the cool wall of the burner lip where they first come into contact in what is known as the liftoff region of the flame. In this region no visible luminescence from the flame is observed. The temperature distribution, the concentration distribution of chemical species, and the velocity distribution in the coflowing geometry are two dimensional since these quantities vary in both the axial and radial direction. Thus, a mathematical analysis of the flowfield of a coflowing diffusion flame is somewhat difficult due to the effects of premixing of reactants near the cold wall, buoyancy, and two dimensionality. Due to mathematical complexity.

utilization of the coflow geometry is not well suited for a comparison of experimental results with the results of asymptotic theory on the structure of diffusion flames. However, an advantage of the coflow system are the large chemical residence times which allows one to follow with high resolution the detailed pyrolysis of the fuel molecules.

A counterflow diffusion flame contains a stagnation point towards which fuel and oxidizer flow from opposite directions. The resulting flame is both flat and thin. In counterflowing systems closer confinement is required for stability, consequently the observation volumes and residence times are smaller when compared to the coflowing configuration. Since the flow velocities in counterflowing systems are considerably higher than those in a coflowing system, forced convective effects dominates over buoyancy. The composition profiles of stable species and temperature profiles are one dimensional (to the leading approximation). This can be shown by theoretical analysis (Fendell, 1965) and has been confirmed by experimental measurements (Seshadri, 1977). Premixing of the reactants other than in the reaction zone does not occur in this configuration.

A diffusion flame which has the oxidizer stream premixed with a small amount of fuel is defined here as a partially premixed, diffusion flame. Few investigators have previously focussed their attention on the extinction of partially premixed, diffusion flames.

2. BACKGROUND

A number of theoretical and experimental studies have been made on the asymptotic structure and mechanisms of extinction of counterflow diffusion flames burning pure fuels (Fendell, 1965, Liñán, 1974, Krishnamurthy *et al.*, 1976, Peters, 1984b). Fendell (1965) analyzed the structure of a steady diffusion flame stabilized in the incompressible, inviscid, stagnation point flow of an oxidizing gas mixture over the surface of a vaporizing condensed fuel. The chemical reaction between the fuel and oxidizer was approximated as a one step irreversible process. By use of numerical integration Fendell (1965) showed that the maximum temperature follows an S-shaped curve when plotted as a function of the Damköhler Number D, when the latter quantity varies from zero to infinity. The Damköhler Number is the ratio of a characteristic flow time to a characteristic chemical reaction time. The corners of the S curve were identified as critical conditions of ignition and extinction. Liñán (1974) analyzed the structure of a diffusion flame stabilized in the inviscid, stagnation region of counterflowing streams of gaseous oxidizer and fuel for the limit of large nondimensional activation temperature. The analysis provided Liñán (1974) criteria for ignition and extinction that could be computed analytically. Krishnamurthy *et al.*, (1976) extended Liñán's analysis to predict extinction of a diffusion flame in an axisymmetric stagnation point boundary layer of a condensed fuel. The predictions of the theory developed by Krishnamurthy *et al.* (1976) were used by Seshadri (1977) to obtain the overall chemical kinetic rate parameters characterizing the gas phase oxidation of a number of liquid and solid fuels in the vicinity of extinction. Considering combustion in stagnation point boundary layers adjacent to condensed fuels, Sohrab (1981) concluded that radiant heat losses from the flame zone had negligible effect on the extinction of gaseous, laminar diffusion flames.

The technique of asymptotic analysis employed in the study of strained, laminar diffusion flames is an attempt to deduce general qualitative results without resorting to extensive numerical computations which may mask the essential physics of the phenomena. In the asymptotic studies reported here, complex flame chemistry is approximated as a one step overall reaction. The fidelity of the one step approximation must be judged through comparison of theoretical predictions with experimental results. For non-premixed flames burning liquid multicomponent fuel blends as described in Chapters III and IV, the one step approximation has been successful in predicting extinction.

In general, previous work on multicomponent fuels has been focussed on the burning rate behavior of free droplet combustion with specific interest in water-oil emulsions (Law, 1976, and Lasheras *et al.*, 1980). These studies, however, did not consider the mechanisms of extinction of multicomponent fuels. At the same time, previous theoretical and experimental analyses of the structure and mechanisms of extinction of laminar diffusion flames, have been concerned with one effective fuel. Thus, a study of the structure and extinction of diffusion flames burning multicomponent fuels and of partially premixed, diffusion flames in the counterflow configuration have a sound theoretical base and can be viewed as an extension of previous work.

For the combustion phenomena studied in this work, both counterflow and coflow configurations are utilized. Chapter II describes the details of the experimental apparatus and discusses the experimental procedures employed. In Chapters III, IV, V, and VI, the counterflow type geometry is used to analyze the asymptotic behavior of diffusion flames burning multicomponent fuels. Chapter III is concerned with the counterflow diffusion flame burning in the stagnation point boundary layer of an evaporating condensed multicomponent fuel. An asymptotic theory is developed which leads to a simplified mixing rule, which can be used to predict the overall chemical kinetic parameters characterizing gas phase oxidation of hydrocarbon/alcohol fuel blends. Experimental results are compared with theoretical predictions. In Chapter IV, an asymptotic theory is developed and it is shown that the critical conditions of extinction of multicomponent diffusion flames can be predicted if the overall chemical kinetic rate parameters characterizing the gas phase oxidation of pure fuels are known. Experimental results are compared to theoretical predictions. In Chapter V, the influence of alcohols on the combustion of hydrocarbon fuels is evaluated. An examination of the detailed structure of a diffusion flame lends insight into the chemical mechanisms of fuel pyrolysis and oxidation. In Chapter VI, the experimentally determined structure of diffusion flames burning hydrocarbon/alcohol fuel blends is described.

In Chapter VII the counterflow geometry is used to analyze a partially premixed, diffusion flame near extinction. This flame geometry is identical to that of a diffusion flame except that the oxidizing gas is mixed with fuel and effectively becomes a lean premixed combustible. Through the development of an asymptotic theory, the mechanism of extinction of this flame is considered. The overall activation energy of this type of flame is determined experimentally and compared to work by other investigators. Physical arguments are made about the stability of these type of flames.

The formation and emission of soot have long concerned scientists. The generation of soot from a combustor presents a health problem and reflects poor combustion efficiency. It is hoped that through an improved understanding of the processes of soot generation, one may be able to better control soot emissions from combustors. Although a multitude of studies exist in the literature about the formation of soot, many basic questions remain unanswered. Are polyacetylenes or polynuclear aromatic compounds precursors of soot? Are molecular radicals or ions intimately involved with the mechanisms that leads to soot production? Few studies have considered the generation of soot in small flames which are well suited for studies of kinetic processes and mechanisms of soot formation. A comparative study of the structure of overventilated, coflowing, laminar diffusion flames burning diluted ethane, diluted ethylene, and diluted acetylene is considered in Chapter VIII. In the coflow configuration utilized in these experiments one obtains a pyrolysis region which is spatially nine times larger than that of the counterflow geometry described in Chapters III-VI. The large chemical residence times associated with the coflowing system allow one to follow with high resolution the detailed pyrolysis of fuel molecules and facilitates a study of the chemical processes which occur in the flame. In Chapter VIII, the structure of overventilated, coflowing, laminar diffusion flames burning diluted ethane, diluted ethylene, and diluted acetylene are experimentally determined. The results are discussed in terms of the sooting behavior of these fuels. In Chapter IX a method to remove acetone impurities from commercial acetylene gas cylinders is described. The conclusions of this study are summarized in Chapter X.

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CHAPTER II

EXPERIMENTAL APPARATUS AND PROCEDURES

1. THE COUNTERFLOW BURNER APPARATUS

Figure 1 shows a schematic illustration of the counterflow burner assembly which was utilized in the experiments described in Chapters III-VI. The burner shown in Fig. 1 consists of a fuel cup which has a diameter of 45 mm and a depth of 18mm and a gas duct through which gaseous oxidizer may be introduced. The fuel cup is cooled by water at the bottom in order to prevent the fuel from boiling, but is not cooled at the rim as that would establish a radial temperature gradient within the liquid. A narrow annulus surrounds the wall of the cup near the rim to catch any overflow of fuel and prevent it from entering the exhaust duct. Since the flame sheet is very sensitive to surface movements, the fuel height in the cup is accurately controlled by a device similar to that used by Bajpai (1973). A Modification of the Bajpai device was made with the addition of a regulating valve as seen in Fig. 2 allowing for more accurate control of the location of the fuel surface in the fuel cup. A fine pointer projecting up through the liquid pool is used as an aid in adjusting the height of the fuel surface. Satisfactory repeatability has been obtained by setting the pool at the level at which the pointer just forms a discernible dimple on the fuel surface. The gas handling system is designed such that it is possible to introduce gaseous fuel, air and nitrogen (which is essentially inert at the temperatures considered in these studies) from the top duct. The gas duct has an inner diameter of 50.1mm. A number of fine wire screens (200 mesh/inch) are placed in the duct to reduce turbulence and ensure a flat velocity profile at the exit of the duct. Using a hot wire anemometer in a similar apparatus, Sohrab (1981) showed that the velocity fluctuations across the exit plane of the oxidizer duct was on the order of 7% over a wide range of strain rates. It was concluded that the velocity uniformity provided by the screens was satisfactory (Sohrab, 1981). The distance between the ducts is adjustable and the duct can be swivelled to allow access to the fuel cup. The flowrates of air, nitrogen and the fuel are measured by use of variable area flowmeters. Pressure gauges arranged in parallel with the flowmeters insure that the flowrate of the gas stream is not affected by fluctuations in the output pressure of compressed gas cylinders or variation in stagnation pressure when adjusting another component in the gas stream. Whenever possible the flowmeters were calibrated by use of wet test meters. The flowmeters are rated at an accuracy of 3%. Mild suction is used to pull the combustion product gases into a heat exchanger surrounding the fuel overflow rim. The suction minimizes the influence of ambient air currents on the flame, and prevents afterburning in the heat exchanger. It was determined that over the range of experimental parameters used in these studies, the suction did not affect the results. The separation distance between the lips of the ducts is maintained at a constant value equal to 1.0 cm. A carefully machined aluminum block acts as a spacer which can be used to insure that the separation distance between the ducts is uniform and constant.

With a liquid fuel in the cup, one may ignite the fuel and introduce an oxidizing gas from the top duct in order to establish a flat, thin diffusion flame just above the vaporizing surface of the liquid fuel. Figure 3 shows a photograph of a diffusion flame with heptane as fuel. A steady flame similar to that shown in Fig. 3 can be indefinitely stabilized in this apparatus. If a small concentration of fuel is introduced into the oxidizer stream a partially premixed diffusion flame results which will be discussed in detail in Chapter VII of this work. Figure 5 of Chapter VII shows a partially premixed diffusion flame with two reaction zones. The flamelet on top is a fuel lean, premixed flame.

2. THE COFLOW BURNER APPARATUS

Figure 4 is a schematic illustration of the coflow burner. The burner consists of two concentric pyrex tubes. The inner tube has a diameter of 1.5 cm and is 30 cm long. The outer concentric tube has a diameter of 6.5 cm and is 38 cm long. A slot was cut into the outer tube to allow a sampling probe to be introduced along the radial direction. Glass beads were placed at the bottom of both of the concentric tubes to obtain a uniform flow of the gaseous reactants through the burner. The flow rate of fuel nitrogen, and air were measured by use of variable area flowmeters which were calibrated by use of a wet test meter and bubble flowmeters. The entire burner is mounted under a fume hood which provides enough suction to remove nonignited fuel and the products of combustion.

Fuel mixed with nitrogen was introduced into the inner tube and synthetic air was introduced into the outer tube. Synthetic air (a blend of nitrogen and oxygen) should be used in the coflow burner when the fuel is diluted with nitrogen in order to avoid difficulties in determining the quantity of Argon diffusing into the flame cone. Experiments were performed with the velocity of air in the outer concentric cone maintained at a constant value equal to 2 cm/sec. Initially the fuel flow rate was adjusted such that a diffusion flame approximately 2 cm in height can be stabilized in the burner. Nitrogen was then added to the fuel stream gradually. The fuel flow rate was also simultaneously adjusted such that one can stabilize a diffusion flame about 2 cm in height. Figure 5 shows a photograph of an ethylene coflow diffusion flame. The two zone sooting region is visually apparent.

3. GAS SAMPLING SYSTEM

Composition profiles of stable chemical species were measured by use of gas sampling with quartz microprobes and gas chromatographic analysis. Chemical species such as radicals and ions cannot be detected by gas chromatography. In Fig. 6 we show a schematic illustration of the gas sampling system. A quartz microprobe is connected by a flexible heated teflon or glass line to the sampling loop of the gas chromatograph. The quartz microprobe is made using the procedure described by Fristrom and Westenberg (1965). By use of a vacuum pump, a sample is pulled through the quartz microprobe and into the sample loop of the gas chromatograph (GC). If the pressure in the sample loop is low enough, the flow at the tip of the probe is choked and is followed by a supersonic expansion downstream of the throat. The expansion causes the static temperature to drop and chemical reactions to freeze. The quartz microprobe, was mounted on an X-Y positioner. The location of the tip of the probe with reference to the edge of the fuel duct was determined by use of a cathetometer or a dial gauge indicator, both having a reading accuracy of 0.005mm. A quartz microprobe of approximately 120 microns in diameter can be used in flames where no soot is formed. In flames where yellow regions of small soot particles are present, sampling with a microprobe is very difficult due to blockage by soot particles. In such cases it may be possible to use a probe with approximately a 250 micron tip diameter. The flow at the tip of this larger probe will not be choked as care must be taken not to distort the flame by removing a large sample. In coflowing systems the flow velocities are small in comparison to the counterflow systems. Consequently sampling must be done at a slower rate. Experience shows that measurements in a counterflow diffusion flame are easier than those in a coflowing diffusion flame. because the flow velocities in the former configuration are larger. consequently distortion of the flame due to sampling is negligible. For the counterflow experiments described here the mass flow rate was large enough to permit a choked flow in the microprobe. Heating of the quartz probe body itself is recommended as this prevents condensation of low boiling point chemical species in the probe and thereby a more accurate determination of their concentration with the GC.

The gas chromatograph used was a Vista 6000 model manufactured by Varian Instruments. The GC is controlled by a Vista 401 Chromatograph Data System. The Vista 401 is a microcomputer used for data analysis. The chromatograph can accept three columns. although in the analysis reported here only two columns were used on any single run. Figure 7 shows the internal plumbing of the GC. The columns are connected by a tenport valve with a sample loop (VI), a four port valve (V2), and two six port valves (V3 and V4). The GC is mounted with a thermal conductivity detector (TCD). The valves V2, V3, and V4 allow the columns either to be in series with the detector or be bypassed. The ten port valve V1 is used for collecting the sample in the sample loop, injecting the sample into the chromatograph and for backflushing the heavier components of the gas mixture from the columns onto the TCD detector.

Calibration of the instrument was performed using commercially obtained standard mixtures of gases. Calibration of the TCD was accomplished by injecting mixtures of nitrogen and the gas to be tested in known proportions. Calibrated were determined with respect to nitrogen. For chemical species which are liquid at room temperature and atmospheric pressure, a different calibration procedure is necessary. For such species calibration was performed by half filling a leak tight flask with the liquid of interest as shown in Fig. 8. Nitrogen was slowly bubbled through the liquid forcing the saturated nitrogen to pass through a heated glass line into the sample loop of the GC. The pressure in the flask was monitored by a 0-800 torr absolute pressure gauge. It was observed that the pressure inside of the flask did not deviate more than 3 torr from atmospheric pressure. The flask was placed in a constant temperature water bath for stabilizing the temperature of the liquid from fluctuations in room temperature. From the temperature of the water bath one may obtain the partial pressure of the liquid vapor inside the flask from tables (Gallant, 1968). Assuming that the remainder of the pressure is due to nitrogen, calibration of the GC for condensed species was obtained.

A procedure used for obtaining composition profiles of stable chemical species is described below. Before a sample was withdrawn from the flame, the entire sampling line was flushed with helium ~~for a period of 5 minutes. A sample was then withdrawn from~~ the flame at a line pressure of 200 torr in the counterflow configuration and at about 700 torr in the coflow configuration. A sampling time of six minutes was estimated to be sufficient to fill the sampling loop of the GC with a representative sample from the flame. When the sampling period was complete, the shutoff valve on the roughing pump side of the GC sampling loop shown in Fig. 6 was closed as was the valve just downstream of the nozzle. The sample line was then slowly pressurized with helium until the pressure gauge read 760 torr, at which time the sample was injected into the GC.

Two separate runs were used at each data point. Table 1 outlines the elution times of various compounds of interest. The carrier gas used in the GC was helium flowing at a rate of 30 ml min. and the reference gas was also helium flowing at the same rate. These flowrates were maintained a constant value during the experiment. The TCD oven temperature was maintained at 180 ℃ and the current flowing through the filaments was 199 amps. In the first run separation was performed using only a Porapak N column (6 feet in length and 1/8 inch in diameter), denoted as column 2 in Fig. 7, while the other columns were bypassed. The oven was initially maintained at 50 ℃. The sample was injected into the GC and the compounds H_2, $N_2 + CO + O_2$, CH_4, CO_2, C_2H_4, C_2H_6, and C_2H_2 were observed to elute. Ten minutes after injection the oven temperature was raised to 100 ℃ at a rate of 50 ℃ min. The compounds C_3H_6,

C_3H_4 (allene), and C_3H_4 (methyl- acetylene) were observed to elute. Nineteen minutes after injection the temperature was raised to 170 ℃ at a rate of 50 ℃/min. The compounds C_4H_8 (1-butane), C_4H_6 (1,3 butadiene), C_3H_6O (acetone), and C_6H_6 were observed to elute. In this analysis N_2, CO, and O_2 elute as a single peak. To determine the relative concentration of these species a second run must be performed. The second run was performed using a Molecular Sieve 5A column (6 feet in length, 1/8 inch in diameter) in series with a Porapak Q column (6 feet in length, 1/8 inch in diameter), denoted respectively as columns 2 and 3 in Fig. 7. The carrier gas used in the GC was helium flowing at a rate of 80 ml/min, and the reference gas was also helium flowing at a rate of 30 ml/min. These flowrates were maintained a constant value during the experiment. The TCD oven temperature was maintained at 180 ℃ and the current flowing through the filaments was 199 amps. The columns were initially maintained at a temperature of 30 ℃. The sample was injected into the GC and the light species H_2, O_2, N_2, CO and CH_4 were allowed to flow from the Porapak column into the molecular sieve column. At this time, H_2 and O_2 were observed to elute. At 1.9 minutes after injection of the sample, the Porapak column was bypassed in order to trap the heavier compounds inside of it. At 5.5 minutes after injection, the column temperature was increased to 80 ℃ at a rate of 50 ℃/min and the compounds N_2+CH_4 were observed to elute. Since N_2 and CH_4 elute as a single peak in this run the result for concentration of CH_4 obtained in the previous run should be used to obtain the concentration of N_2. At 5.5 minutes after injection, the temperature of the columns was increased to 80 ℃ at a rate of 50 ℃/min and CO was observed to elute. At 11 minutes the Molecular Sieve column was bypassed and the Porapak column was put into series at 11.5 min. The compounds CO_2, C_2H_4 + C_2H_2, and C_2H_6 were observed to elute. At 14 minutes after injection of the sample, the temperature of the columns was increased to 120 ℃ at a rate of 50 ℃/min and the compounds H_2O, C_3H_6, CH_2O, and CH_3OH were observed to elute. After 17.5 minutes, the temperature of the columns was increased to 220 ℃ at a rate of 50 ℃/min. The compounds C_7H_8 and C_7H_{16} were observed to elute. After completing a run, if condensed water or deposits of soot were observed in the microprobe, then they were dispelled by temporarily heating the probe externally with a bunsen burner, and removing the products by use of a vacuum pump. It has been observed that argon elutes with oxygen in the gas chromatograph when using the conditions described above. A method for correcting the concentration of oxygen is outlined by Seshadri (1977) and necessitates the assumption that the diffusion coefficients of argon and nitrogen are equal.

4. TEMPERATURE MEASUREMENTS

Temperature profiles were measured by using platinum versus platinum-10% rhodium thermocouples of 0.0508 mm wire diameter. The thermocouples were coated with a layer of SiO_2 or Yttrium Oxide to prevent catalytic heating effects (Kent, 1970). Corrections for radiant heat losses from the thermocouple bead were made by use of a method described by Seshadri and Rosner (1984). In yellow or sooting flames deposition of soot on the thermocouple bead occurred. Therefore, data was obtained during a certain time interval and the result was extrapolated to the time of insertion of the thermocouple into the sooting flame zone (Saito *et al.*, 1985).

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PORAPAK N ELUTION TIMES

TIME (min.)	SPECIES
0.75	H_2
0.84	N_2, CO, O_2, Ar
1.26	CH_4
3.38	CO_2
4.45	C_2H_4
5.49	C_2H_6
8.31	C_2H_2
13.4	C_3H_8
14.4	C_3H_6
16.2	C_3H_4 (allene)
18.1	C_3H_4 (methyl-acetylene)
20.8	C_4H_{10}
21.4	C_4H_8 (1-Butene)
21.7	C_4H_6 (1,3 Butadiene)
22.3	C_4H_4 (vinyl acetylene)
22.5	water
23.8	C_4H_2 (diacetylene)
27.5	acetone
38.3	benzene

TABLE 1

Elution times of chemical species on the gas chromatograph from a Porapak N packed column using the procedure described in the text.

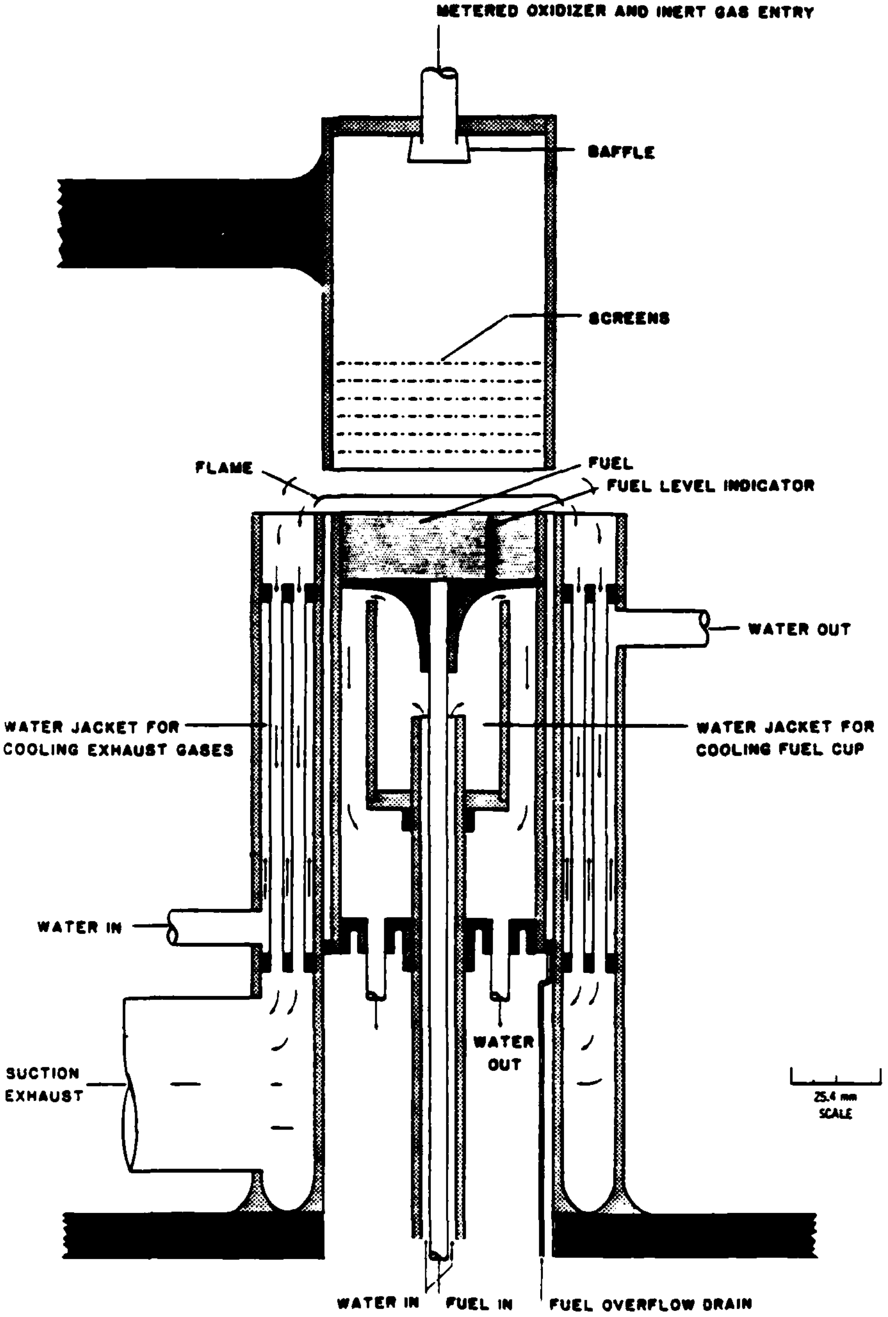

FIGURE 1

Schematic illustration of a counterflow burner.

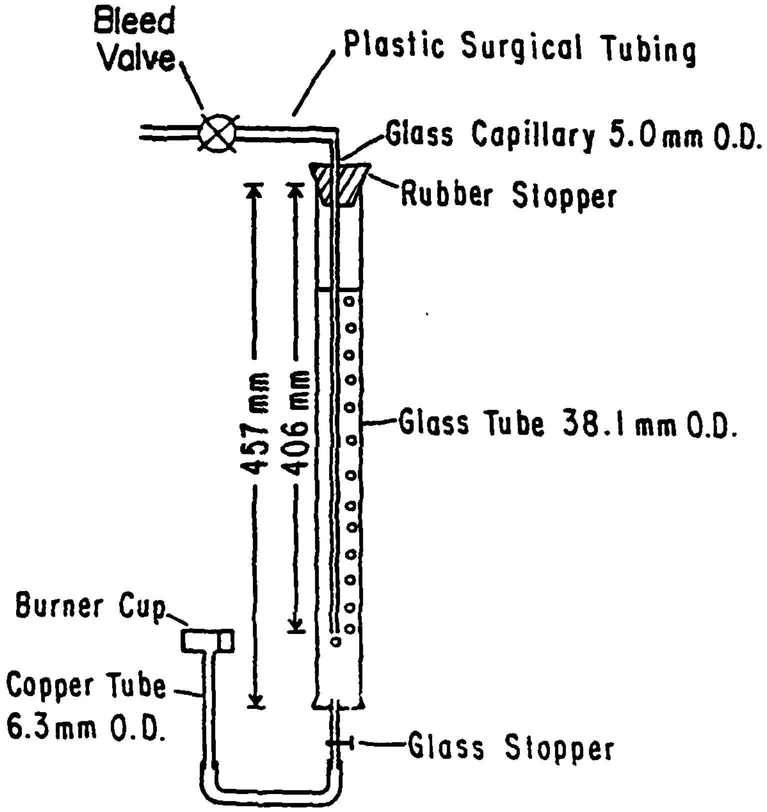

FIGURE 2

Line drawing of the modified Bajpai device used to adjust the location of the fuel surface in the fuel cup for the counterflow liquid fuel burner.

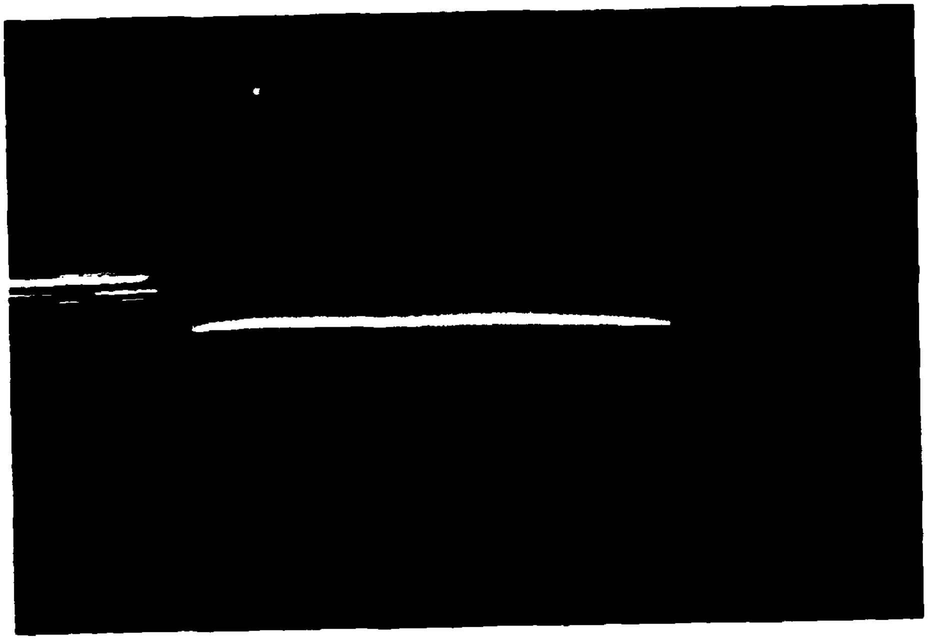

FIGURE 3

Photograph of a diffusion flame burning heptane.

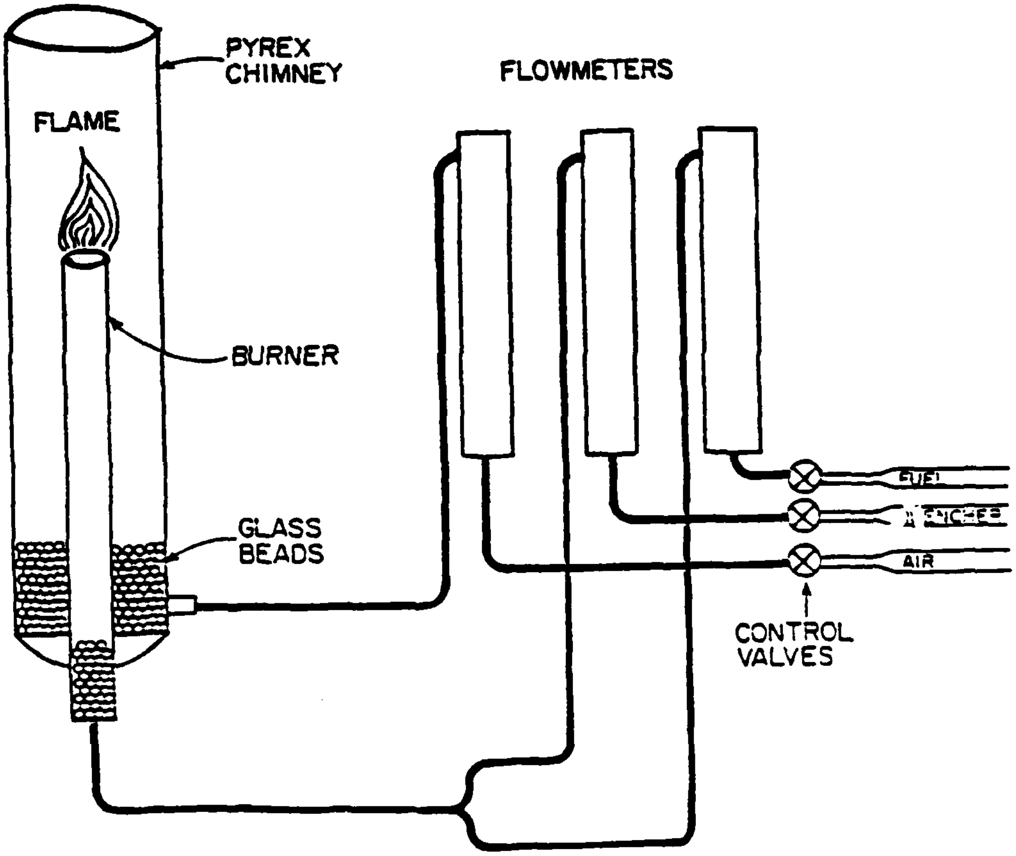

FIGURE 4

Schematic illustration of the coflowing burner apparatus.

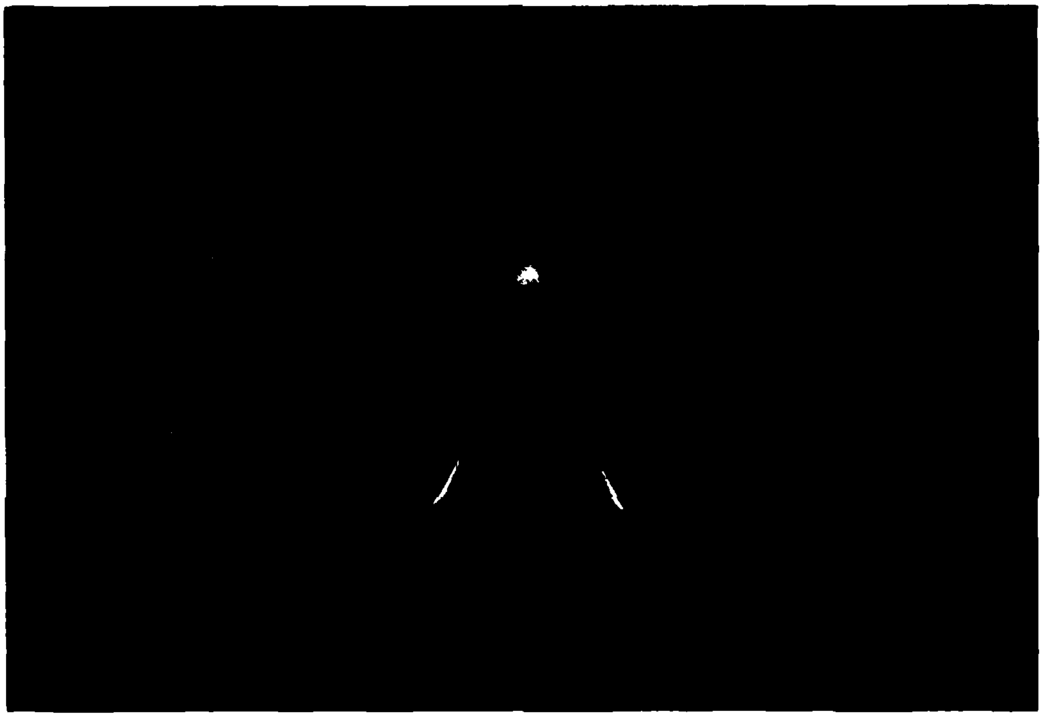

FIGURE 5

Photograph of a coflow diffusion flame. Fuel = 13.9% Ethylene + 86.1% Nitrogen. Fuel velocity = 1.01 cm/sec.

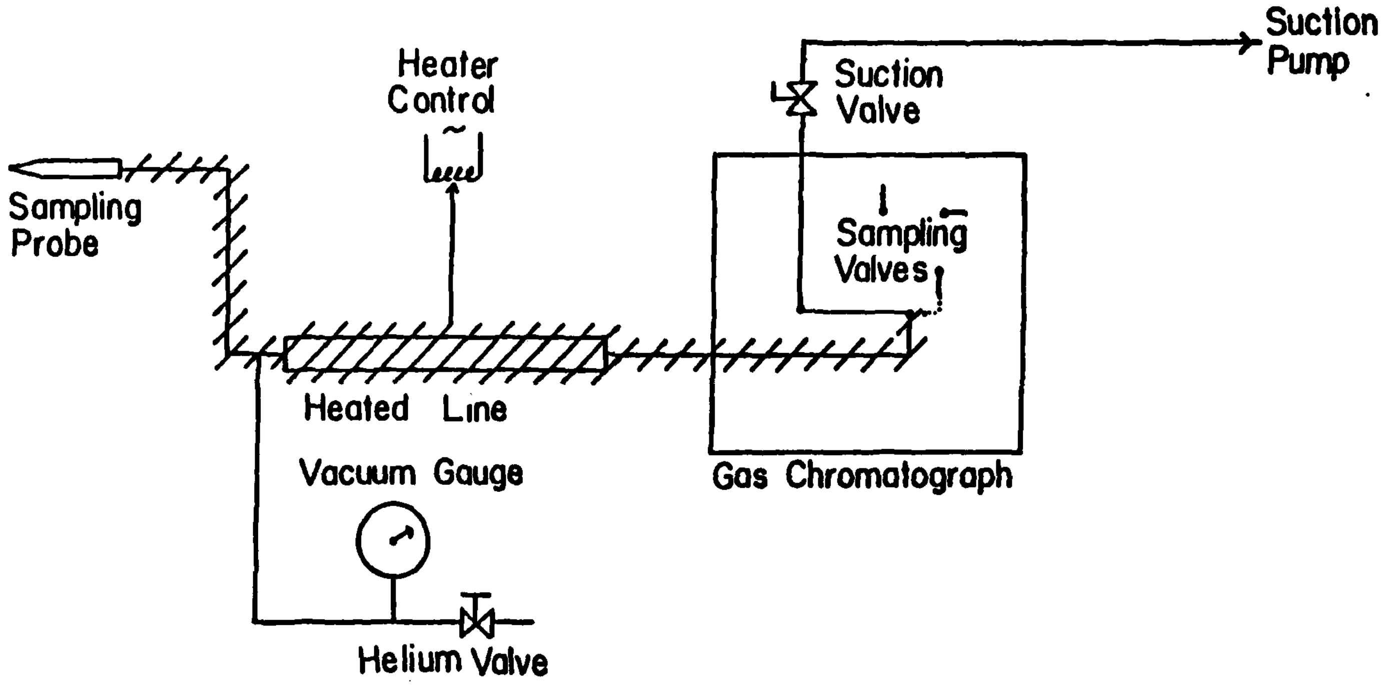

FIGURE 6

Schematic illustration of the sampling system.

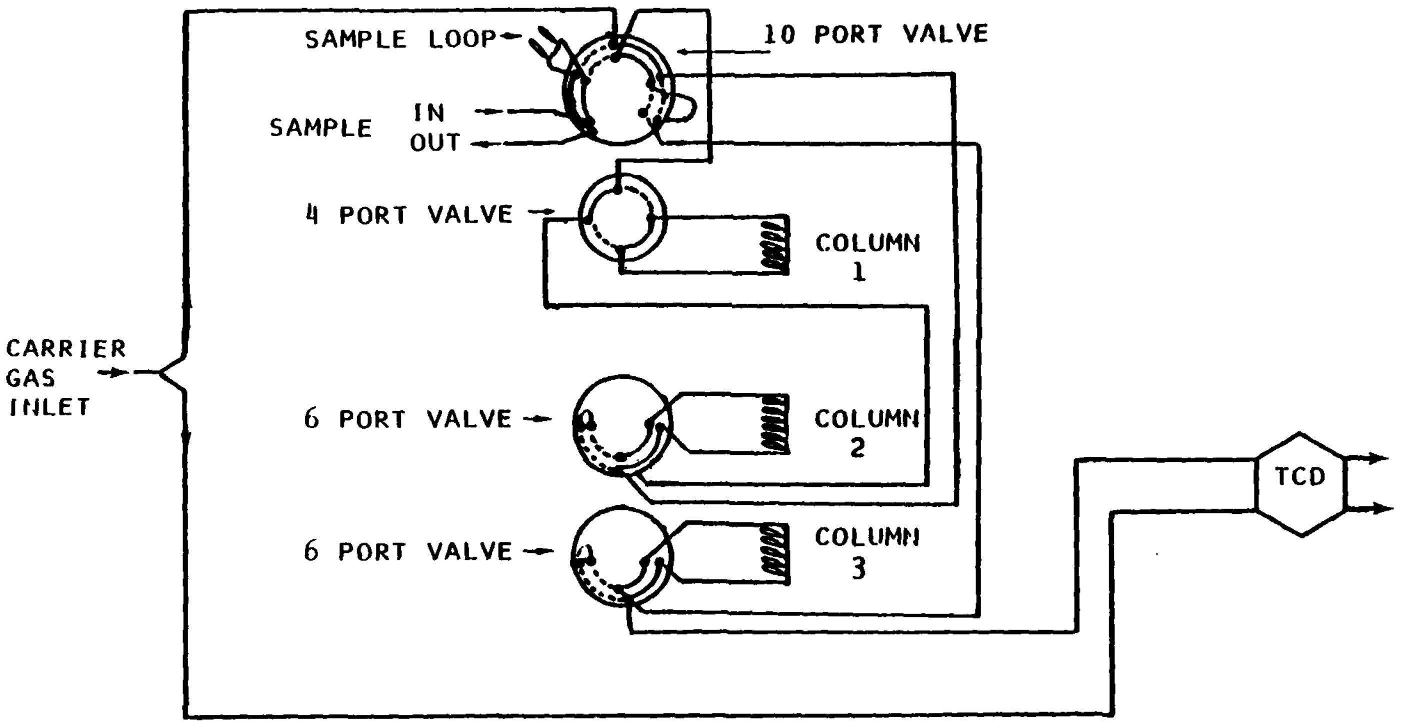

FIGURE 7

Schematic illustration of the internal plumbing system in the gas chromatograph.

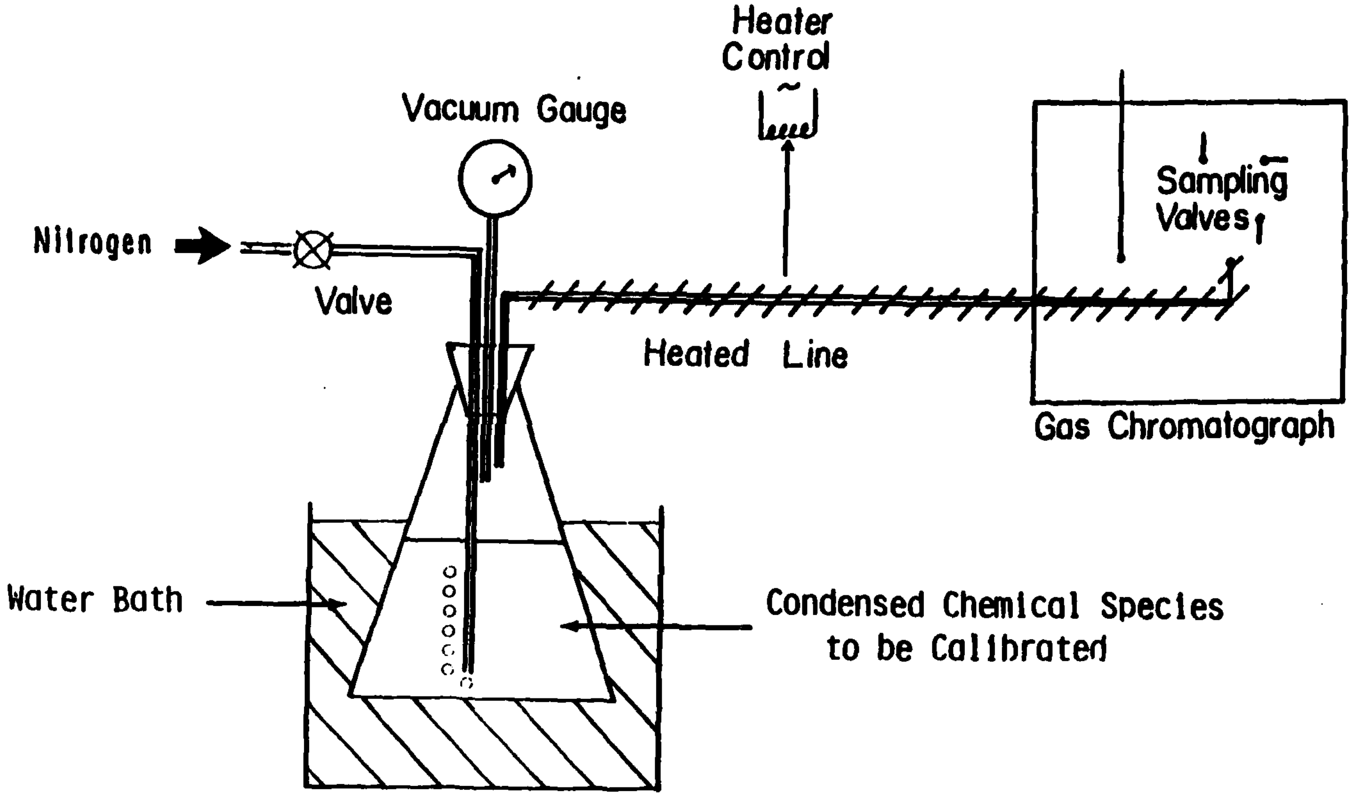

FIGURE 8

Schematic illustration of the apparatus for the calibration of condensed species by the gas chromatograph.

CHAPTER III

PREDICTION OF OVERALL CHEMICAL KINETIC RATE PARAMETERS NEAR EXTINCTION FOR DIFFUSION FLAMES BURNING MULTICOMPONENT FUELS

ABSTRACT

A mixing rule is developed to predict extinction of a diffusion flame burning a multicomponent fuel. The chemical reaction is approximated as a one step process between each component of the fuel and the oxidizer, and the activation energy characterizing the reaction is presumed to be large. The mixing rule predicts the overall chemical kinetic rate parameters characterizing the gas phase oxidation of the multicomponent fuel, if the rate parameters for its components are known. To test the validity of the predictions, extinction experiments were performed on diffusion flames stabilized above heptane, toluene, methanol, and a number of homogeneous solutions (with different proportions of the components) of these fuels. Experimental and theoretical values for the overall activation energy for the solutions were found to agree to better than 5%, and the preexponential factors were found to agree to better than a factor of three.

A detailed description of the research summarized above has been published in Combustion Science and Technology 38, 89-104, 1984. The authors of the publication are Dr. A. P. Hamins and Dr. K. Seshadri.

CHAPTER IV

STRUCTURE OF COUNTERFLOW DIFFUSION FLAMES BURNING MULTICOMPONENT FUELS

ABSTRACT

The structure of a diffusion flame stabilized between counterflowing streams of a multicomponent fuel containing N components and an oxidizing gas stream is analyzed. It is presumed that each component of the fuel reacts only with the oxidizer, and does not influence the kinetics of pyrolysis or oxidation of the other components. The chemical reaction between each component of the fuel and the oxidizer is approximated as a one-step process with the activation energy for the reaction being large in comparison to the thermal energy in the flame. The near equilibrium regime is analyzed. The equation governing the inner reaction zone is integrated to obtain an explicit analytical expression for the Damköhler number at extinction. It is shown that the critical conditions of diffusion flame extinction (i.e. velocity gradient and oxidizer concentration in the oxidizing stream) for multicomponent fuels can be predicted if the overall chemical kinetic rate parameters characterizing the gas phase oxidation of single component fuels are known. To test the validity of these predictions, experiments were performed on diffusion flames stabilized above heptane, toluene, methanol and a number of homogeneous solutions (with different proportions of the components of these fuels). For solutions of heptane and toluene the theoretical predictions were found to be in excellent agreement with the experimental measurements. However, for solutions of methanol with toluene and for solutions of heptane, toluene and methanol, the theoretical predictions were slightly different from the experimental measurements. It is suggested that the discrepancy may be due to chemical modification of pyrolysis and/or oxidation mechanisms of hydrocarbon fuels by methanol or vice versa.

A detailed description of the research summarized above has been published in the Twentieth Symposium (International) on Combustion, The Combustion Institute, 1905-1913, 1984. The authors of the publication were Dr. A. P. Hamins and Dr. K. Seshadri.

CHAPTER V

THE INFLUENCE OF ALCOHOLS ON THE COMBUSTION OF HYDROCARBON FUELS IN DIFFUSION FLAMES

ABSTRACT

A theoretical and experimental investigation of the influence of alcohols on the critical conditions of extinction of diffusion flames burning hydrocarbon fuels is outlined here. Experiments were performed on diffusion flames stabilized between the vaporizing surface of a liquid fuel and an oxidizing gas mixture. Liquid fuels tested were heptane, toluene, methanol, ethanol, and butanol, and a number of homogeneous solutions of these fuels in different proportions. Experimental results were interpreted by use of an asymptotic theory in the limit for a large value for the activation energy characterizing the gas phase chemical reaction between each component of the fuel in the fuel solution and the oxidizer when compared to the thermal energy in the flame. The theory was used to compare the relative reactivities of pure fuels and fuel mixtures. The influence of alcohols (methanol, ethanol, and butanol) on the reactivities of hydrocarbon fuel solutions was evaluated by this method. Results show that methanol is more reactive than ethanol or butanol. Results on pure fuels show that toluene is less reactive than heptane, ethanol, butanol and methanol. It was observed that the reactivity of a fuel solution containing heptane and toluene increased with increasing proportion of methanol.

A detailed description of the research summarized above will appear in Combustion and Flame, in early 1986. The authors of the publication were Dr. A. P. Hamins and Dr. K. Seshadri.

CHAPTER VI

THE STRUCTURE OF DIFFUSION FLAMES BURNING PURE, BINARY AND TERNARY SOLUTIONS OF METHANOL, HEPTANE AND TOLUENE

ABSTRACT

The structure of counterflow diffusions flames burning methanol, heptane, toluene, binary solutions of methanol and toluene, and heptane and toluene, and ternary solutions of methanol, heptane and toluene is characterized in the vicinity of extinction. Composition profiles of stable species were measured in these flames by use of gas sampling with quartz microprobes and analysis by use of on-line, two column gas chromatography. Temperature profiles were measured by use of coated thermocouples. A number of compounds were observed during pyrolysis of the fuel. Experimental results were analyzed by using the mixture fraction (conserved scalar) as the independent variable. Results show that for a diffusion flame burning heptane the approximation that the Lewis number for all species are approximately equal to unity is valid. When the composition profiles for major chemical species and temperature profiles are plotted with mixture fraction as the independent variable, the maximum value of the concentration of the major stable species and the maximum value of the temperature were found to occur on the rich side of stoichiometry. For diffusion flames burning solutions of methanol, heptane and toluene, the composition of the hydrocarbon fuels were observed to extrapolate to a value of zero at nearly the same location, however methanol was observed to extrapolate to a value of zero at a different location. It is suggested that a previously developed theoretical analysis which did not allow the fuel concentrations to attain a value of zero at different locations may give slightly inaccurate results. when used to predict flame extinction.

1. INTRODUCTION

Since the petroleum reserves of the world are limited, there is a need to develop alternate fuels which can be readily obtained from plentifully available raw materials. Although, the ultimate objective is to replace petroleum as the major automotive fuel, a near term practical approach is to mix petroleum derived fuels with nonpetroleum derived fuels and thus extend the use of hydrocarbon fuels. Blends of methanol and ethanol with hydrocarbon fuels have been suggested as a possible approach to extending the availability of liquid petroleum based fuels [1,2]. Therefore, fundamental studies on the influence of alcohol on combustion of hydrocarbon fuels are relevant. Here we present results of experimental investigation of the structure of diffusion flames burning solutions of alcohol fuels and hydrocarbon fuels. Petroleum based fuels are normally a blend of aromatics, olefins and saturates. The concentration of components in the blend depend on the fuel and its grade. A well defined laboratory study necessitates control of the fuel composition. Thus, experiments were performed using heptane, toluene, methanol and homogeneous solutions of heptane/toluene, toluene/methanol and heptane/toluene/methanol. The experimental configuration used was the counterflow, diffusion flame stabilized by directing an oxidizing gas stream downward on the burning surface of the liquid fuel. Data obtained were the composition profiles of various stable species in the flame measured by gas sampling and gas chromatographic analysis, and temperature profiles measured by use of coated thermocouples.

Previous studies on combustion of solutions of hydrocarbon and alcohol fuels were concerned with measuring and predicting extinction limits of diffusion flames stabilized above the vaporizing surface of these fuels [3-5]. A mixing rule was developed [3] to predict the critical conditions of extinction of a multicomponent fuel if the critical condition of extinction of the individual components in the fuel blend are known. Later an asymptotic theory was developed from first principles to predict critical conditions of extinction of multicomponent fuels [4]. The chemical reaction between each component of the fuel and the oxidizer was approximated as a one-step process with the activation energy for the reaction being large in comparison with thermal energy of the flame [4]. The theory gives an explicit analytical expression for the Damköhler number at extinction. The Damköhler number being defined as the ratio of a characteristic flow time to a characteristic chemical reaction time. It was shown that the critical conditions of extinction of a diffusion flame (i.e. velocity gradient and oxidizer concentration in the oxidizing stream) for multicomponent fuels can be predicted if the overall chemical kinetic rate parameters characterizing the gas phase oxidation of single component fuels are known [4]. For solutions of heptane and toluene the theoretical predictions of extinction of diffusion flames were in excellent agreement with experimental measurements [4]. For solutions of methanol and toluene and for solutions of heptane, toluene and methanol, the theoretical predictions of extinction of diffusion flames were slightly different from the experimental measurements [4]. The theory was also used to compare the relative reactivities of various pure fuels and fuel solutions in the vicinity of extinction [5]. By using data for critical conditions of extinction of diffusion flames stabilized above fuel solutions, it was shown that the extinction behavior of gasoline can be modelled as a blend of heptane and toluene [5]. Results showed that methanol was more reactive than heptane and toluene [5]. It was also observed that the reactivity of a fuel solution containing heptane and toluene increased with increasing proportion of methanol.

To obtain an improved understanding of the kinetic, and heat and mass transfer processes occurring in a diffusion flame burning multicomponent fuel in the vicinity of extinction, the flame structure was characterized in detail. Here we show composition profiles for various stable species in the flame measured by gas sampling and gas chromatographic analysis, and temperature profiles measured by use of coated thermocouples. The experimental procedure is described in section 2. In section 3 the experimental results are discussed. Our conclusions are summarized in section 4.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

A diffusion flame can be stabilized in a counterflow configuration in the stagnation point boundary layer over the surface of a vaporizing condensed fuel. A schematic illustration of the burner and description is given in Chapter II. For a diffusion flame stabilized in a counterflow geometry, there are two independent experimental parameters by which one may control the Damköhler number and thereby the structure of the flame. One parameter is the mass fraction of oxygen in the oxidizer stream which determines the maximum flame temperature and thereby the chemical reaction time, and the other parameter is the velocity of the oxidizer jet at the injection plane which determines the rate of strain (or the stagnation point velocity gradient) and thereby the characteristic flow time. To facilitate comparisons of the structure of diffusion flames, experiments were performed with the rate of strain nearly the same, and the oxidizer mass fraction adjusted such that the Damköhler number is close to its value near extinction. It has been shown previously [6] that the strain rate is equal to V/L where V is the velocity of oxidizer stream near the injection plane and L is the distance between the tip of the liquid fuel cup and the tip of the oxidizer duct [3].

Temperature measurements were made with Pt vs. Pt.-10% Rh thermocouples with a wire diameter of 0.0254 mm. The thermocouples were coated with a layer of yittrium oxide to prevent catalytic chemical reactions from occurring on their surface. Temperature measurements were corrected for radiative heat losses by using a previously developed procedure [7]. The radiation correction at the peak flame temperature was about 100 ℃ . Conductive heat losses from the thermocouple bead were minimized by positioning the thermocouple wires along an isotherm.

Measurements of composition profiles of stable species in the flame were made by use of gas sampling with quartz microprobes and analyzed by use of on line two column gas chromatography. The quartz microprobe was made [8] with a throat diameter of approximately 120 microns (see Chapter II). Figure 1 shows a schematic illustration of the gas sampling system. The sampling line was made partly with teflon and partly with glass. The microprobe was mounted on an x-y positioner with a micrometer which allowed us to determine the location of the tip of the probe with reference to the oxidizer duct within an accuracy of 0.01 mm. A vacuum pump was used to reduce the pressure in the sample line low enough to cause the flow of the gas at the tip of the nozzle to be choked. The reduced pressure causes a supersonic expansion to occur downstream of the nozzle tip and the static temperature to drop low enough for the chemical reactions to freeze [8]. The sample line was wound with heating tape and the surface temperature was maintained at 80 ℃ to avoid condensation of compounds with low boiling points. It is well known that air obtained from compressed gas cylinders contains Ar as an impurity, and Ar elutes with O_2. Therefore, the results for oxygen were corrected to account for Ar, and the concentration of Ar was included with nitrogen. The gas handling system and the procedures used for gas analysis are described in detail in Chapter II.

3. DISCUSSIONS OF EXPERIMENTAL RESULTS

Composition profiles of stable species and temperature profiles were measured in a number of diffusion flames burning methanol, toluene, heptane, and binary and ternary solutions of these fuels. The conditions for which these measurements were made are shown in Table 1, and the profiles are shown in Figs. 1-7. The experiments were performed at conditions close to flame extinction, and attempts were made to keep the flow velocity of the oxidizer, and consequently the rate of strain nearly the same, with the oxidizer mass fraction within 2% of its value at extinction. In diffusion flames burning toluene a wide sooting zone was observed on the fuel side of the flame sheet. It was not possible to withdraw a sample using the microprobe in the fuel rich region below the flame sheet because soot was found to block the entrance to the probe (see Fig. 2). However when heptane or methanol is added to toluene the yellow zone disappears and it is possible to withdraw a sample with the microprobe in the fuel rich region (see Figs. 4-7). In Figs. 1-7 the position marked 0 represents the location of the luminous flame zone. The composition profiles show that pyrolysis of methanol, heptane, and solutions of methanol, heptane and toluene yields a number of products. The presence of all these products can be explained by examining postulated mechanisms for pyrolysis and oxidation of hydrocarbon and alcohol fuels [9-11]. Figures 6 and 7 show that the concentration of methanol at the luminous flame zone is larger than that of heptane and toluene. To make the point clearer, Fig. 8 shows the ratio of the mole percentage of unburnt fuel to its value in the original fuel solution, as a function of location in the flame using the data shown in Fig. 7. Results show that the normalized concentration of methanol in the flame sheet is larger than that of toluene and that the normalized concentration of toluene in the flame sheet exceeds that of heptane. This observation may be related to the fact that the coefficient of diffusion for methanol is larger than that for toluene which in turn is larger than that for heptane. In addition, the profiles are influenced by the rate of pyrolysis and oxidation of these fuels. Figure 9 compares measured temperatures with the temperature calculated from the measured composition of the chemical species in the flame assuming local adiabaticity for a fuel solution containing 40% heptane and 60% toluene (see Fig. 5). The results shown in Fig. 9 are in fairly good agreement. However, if similar comparisons are made using the data shown in Fig. 1-7 there is good agreement for certain fuels, whereas for fuel solutions containing methanol the peak temperatures differ by almost 300 °C.

It is useful to discuss results for the composition profiles with the mixture fraction as the independent variable. The use of the mixture fraction to analyze data on the structure of diffusion flames has been used previously by Bilger [12] and was later modified by Peters [13]. Here we shall use the latter definition. For the case where the ambient fuel stream does not contain oxidizer and the ambient oxidizer stream does not contain fuel $Z = Z_F/Y_{F,1}$ where $Z_F = Z_{C,F} + Z_{H,F} + Z_{O,F}$. Here $Z_{j,F}$ is the mass fraction of element j contained in the pure fuel, at any location, $Y_{F,1}$ is the mass fraction of fuel in the fuel stream, the subscripts C, H and O denote respectively the elements carbon, hydrogen, and oxygen, and F denotes the fuel. The quantity $Z_{j,F} = \sum_{i=1}^{N} (a_{ij} M_j Y_i)/M_i$ where a_{ij} is a stoichiometric coefficient denoting number of atoms of element j in a molecule of species i, and M denotes the molecular weight. The mixture fraction Z is a conserved scalar, because chemical elements are conserved during chemical reactions. Similarly one can define $\bar{Z} = 1 - Z_O/Y_{O,2}$ where $Z_O = Z_{O,O}$ and $Y_{O,2}$ is the mass fraction of the oxidizer in the oxidizer stream. It can be easily verified that $Z = \bar{Z} = 1$ in the pure, ambient fuel stream and $Z = \bar{Z} = 0$ in the pure, ambient oxidizer stream. Bilger's [12] definition of the mixture fraction for the case considered here is $\hat{Z}_k = Z_{k,F}/Z_{k,F,1}$ where $Z_{k,F}$ is the mass fraction of element k (carbon or hydrogen) contained in the pure fuel at any location, and $Z_{k,F,1}$ is the value of $Z_{k,F}$ at the pure, ambient fuel stream. For fuels containing only carbon and hydrogen if the Lewis number for all species are equal to unity [13] then everywhere $Z = \bar{Z} = \hat{Z}_C = \hat{Z}_H$. Using the data shown in Fig. 3 the various definitions of mixture fraction are plotted in Fig. 10 as a function of distance from the luminous flame zone. The quantity $Y_{F,1}$ is set equal to unity which is equivalent to the hypothetical case where only fuel vapors exist at ambiance. Figure 10 shows that all definitions of mixture fraction give nearly the same value, consequently we can conclude that $Le_i = 1$ for $i=1, \cdots n$ is a good approximation for a diffusion flame burning heptane. For fuels containing oxygen a difficulty arises in distinguishing at any location the fraction of oxygen which was originally in the fuel molecule and the fraction that was originally in the oxidizer. One approach is to set $Z'_{O,F} = 16\alpha_O Z_{C,F}/(12\alpha_C)$ and define $Z' = Z_{H,F} + Z_{C,F} + Z'_{O,F}$ or set $Z''_{O,F} = 16\alpha_O Z_{H,F}/\alpha_H$ and define $Z'' = Z_{H,F} + Z_{C,F} + Z''_{O,F}$. Here α_O, α_C, and α_H represent the number of atoms of oxygen, carbon, and hydrogen in the fuel molecule. Consequently, we can define $\bar{Z}' = 1 - (Z_O - Z'_{O,F})/Y_{O,2}$ or $\bar{Z}' = 1 - (Z_O - Z''_{O,F})/Y_{O,2}$. Anticipating that the carbon based definition of mixture fraction, namely Z' and $\bar{Z}'$ is more accurate than the hydrogen based definition of mixture fraction namely Z'' and $\bar{Z}''$ in Fig. 11 we have plotted Z, $\bar{Z}$, Z', and $\bar{Z}'$ using the data shown in Fig. 1 for a diffusion flame burning methanol. Differences in these curves can be attributed to differences in diffusion coefficients between the various chemical species in the flame. The problem of water buildup in the fuel cup due to back diffusion in the flame is also apparent.

In Fig. 12 we have replotted the temperature and composition of major species in terms of mass fractions using data shown in Fig. 3 for heptane, as a function of Z. It has been shown [13] that the flame position in terms of the mixture fraction Z, for $Y_{F,1} = 1$ is given by the relation $Z_{ST} = Y_{O,2}/[(\gamma'_O M_{O_2}/\gamma'_F M_F) + Y_{O,2}]$ where γ'_{O_2} and γ'_F are coefficients respectively denoting the number of moles of oxygen and the number of moles of fuel required for stoichiometric combustion, and M_{O_2} and M_F respectively are the molecular weights of oxygen and fuel. For the heptane diffusion flame considered here, $Z_{ST} = 0.046$. In Fig. 12 the maximum flame temperature occurs at $Z = 0.081$, which is on the rich side of stoichiometry, similarly the maximum values for concentration of the species CO, CO_2, H_2O and H_2 also occur on the rich side of stoichiometry. In Table 2, Z_{ST} and the location of the maximum temperature are listed in terms of Z for the profiles shown in Figs. 1 and 3-7. Table 2 shows that for all the cases considered here the peak temperature occurs on the rich side of stoichiometry.

Finally in Fig. 13 we have plotted results for major species in terms of mass fractions and temperature for data shown in Fig. 7, with Z as the independent variable. At this condition the stoichiometric mixture fraction occurs at $Z_{ST} = 0.059$, while the maximum flame temperature occurs at $Z = 0.065$. Fig. 13 shows that the fuels, namely heptane, toluene and methanol leak toward the lean side of Z_{ST}, and that the oxidizer leaks toward the rich side of Z_{ST}. The profiles of the fuels in Fig. 13 are nearly straight lines which is consistent with theoretical predictions [13]. In addition, the concentration of heptane and toluene extrapolate to zero concentrations at a value of the mixture fraction that are similar, namely $Z = 0.055$ and $Z = 0.061$ respectively. The concentration of methanol, however, extrapolates to a value of zero at $Z = 0.038$. Similar behavior is observed if data shown in Fig. 6 is reduced with Z as the independent variable. In a previously developed asymptotic theory [4] to predict extinction of diffusion flames burning multicomponent fuels it was assumed that in the outer structure the concentration of all fuels was zero at $Z = Z_{ST}$. It was found that [4] there was excellent agreement between theoretical predictions and experimental results for diffusion flames burning heptane, and toluene, and small systematic deviations occurred between theoretical predictions and experimental results for fuel solutions of toluene and methanol and fuel solutions of heptane, toluene and methanol. Results shown in Fig. 13 suggest that the assumption that the concentration of all fuels are zero at $Z = Z_{ST}$ is not necessarily valid for solutions of hydrocarbon and alcohol fuels.

A more satisfactory analysis of the data presented in Figs. 1-7 would require the development of asymptotic theories using multistep chemical kinetic models, and a comparison of predictions with experimental results. In addition the measured composition profiles for stable and measured temperature profile must be compared with numerical solutions of the conservation equations of motion, energy, and species and using detailed chemical kinetics similar to that performed by Dixon-Lewis *et al.* [14] for methane-air diffusion flames.

4. SUMMARY AND CONCLUSIONS

The structure of counterflow diffusion flames burning methanol, heptane, toluene, binary solutions of toluene and methanol, and heptane and toluene, and ternary solutions of methanol, heptane and toluene is characterized in the vicinity of extinction. In these flames composition profiles of stable species were measured by use of gas sampling with quartz microprobes and analysis by use of on-line, two column gas chromatography. Temperature measurements were made by use of coated thermocouples. In Table 1 we show conditions for which the measurements were made, and the results are shown in Figs. 1-7. The following remarks summarizes our major conclusions.

A number of compounds were observed during pyrolysis of these fuels and their presence can be explained by examining previously postulated chemical kinetic mechanisms for pyrolysis and oxidation of hydrocarbon fuels [9,10], and alcohol fuels [11]. The data shown in Figs. 1-7 are discussed using the mixture fraction [13] as the independent variable. The various definition of mixture fraction as introduced by Bilger [12] and Peters [13] were found to be in agreement if data obtained for heptane (Fig. 3) is analyzed. This implies that $Le_i = 1$ for $i = 1, \cdots n$ is a valid approximation for this case. However the various definitions of mixture fraction were not in agreement if data obtained for methanol (Fig. 1) is analyzed. Data for concentration of major species and temperature shown in Fig. 3 were replotted in Fig. 12 with Z as the independent variable. Figure 12 shows that the position of maximum temperature is on the rich side of stoichiometry. A similar observation was made for the profiles shown in Figs. 1 and 3-7 and the results are tabulated in Table 2. Data shown for the composition of major species and temperature in Fig. 7 were replotted with Z as the independent variable in Fig. 13. The results show that the concentration of heptane and toluene extrapolate to a value of zero at nearly the same value of Z and that this value of Z exceeds the value at which methanol extrapolates to a value of zero. Consequently, it is suggested that a previously developed asymptotic theory [4] where it is assumed that the concentration of all fuels are zero at $Z = Z_{ST}$, can predict extinction of diffusion flames burning solutions of hydrocarbon fuels reasonably accurately. However, if the components of a fuel blend do not attain a zero concentration at a similar flame location, inaccuracies may arise if the results of the asymptotic theory [4] is used to predict extinction of diffusion flames burning fuel blends which have greatly differing leakage rates through the flame zone.

A more satisfactory analysis of the data presented in Fig. 1-7 would be to compare the experimental measurements with predictions of asymptotic theories using multistep chemical kinetic models, and with numerical solutions utilizing detailed chemical kinetic mechanisms.

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Figure number	Fuel Solution Composition (Volume Percent)			Oxidizer		Fuel
	Methanol	Toluene	Heptane	Concentration Y_{o_2}	Velocity U cm/sec	Burning Rate gm/min
1	100	0	0	.150	42.2	0.27
2	0	100	0	.202	34.6	0.80
3	0	0	100	.170	41.2	0.66
4	20	80	0	.179	39.1	0.48
5	0	60	40	.181	39.6	0.56
6	10	36	54	.174	41.2	0.61
7	20	32	48	.161	38.9	0.44

TABLE 1

Conditions for which measurements were made for composition profiles of stable species and temperature profile in diffusion flames.

FUEL COMPOSITION (VOLUMETRIC)	Z_{ST}	Z_{Tmax}
HEPTANE	0.0461	0.0808
METHANOL	0.0984	0.112
20% METHANOL + 80% TOLUENE	0.0595	0.125
40% HEPTANE + 60% TOLUENE	0.0526	0.0658
10% METHANOL + 54% HEPTANE +36% TOLUENE	0.0487	0.0765
20% METHANOL + 48% HEPTANE + 32% TOLUENE	0.0588	0.0646

TABLE 2

Value of Z_{ST} and location of the maximum value of the peak temperature for profiles shown in Figs. 1-7.

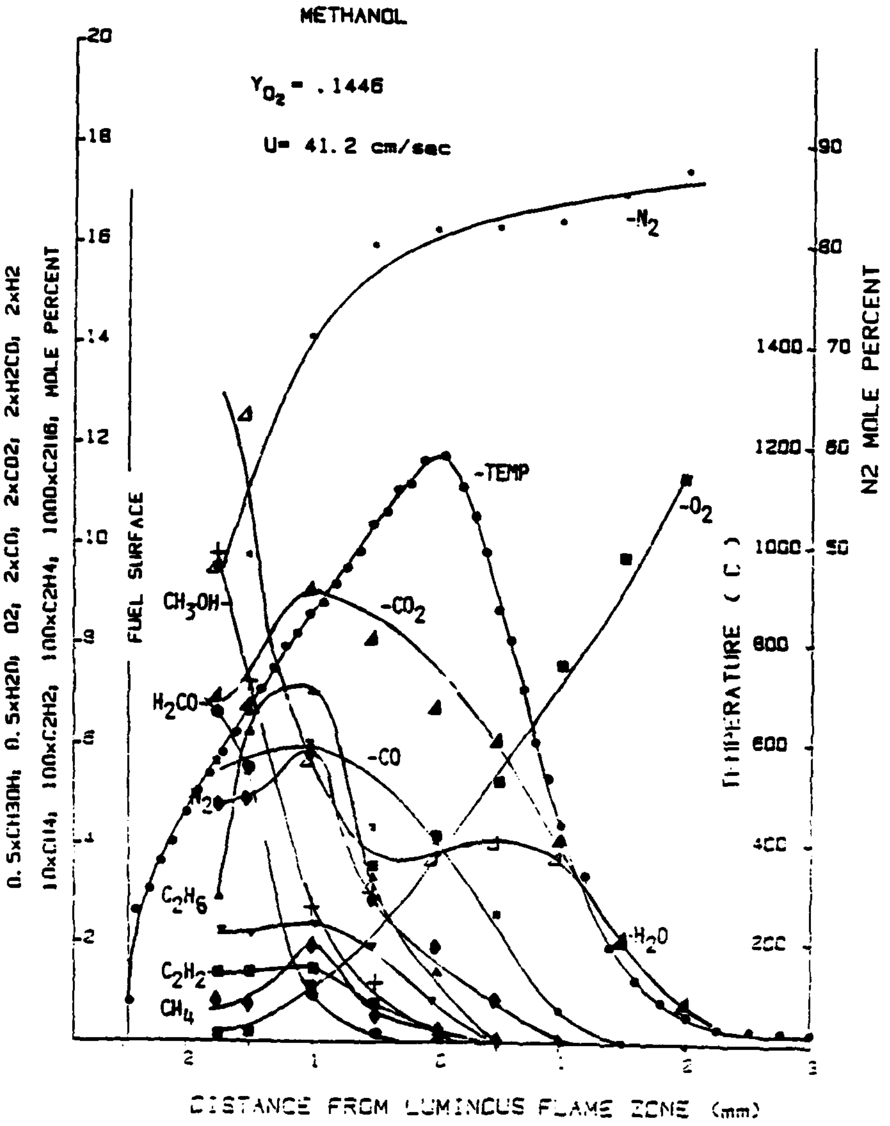

FIGURE 1

Composition profiles of stable species and temperature profile in a diffusion flame above a burning pool of methanol.

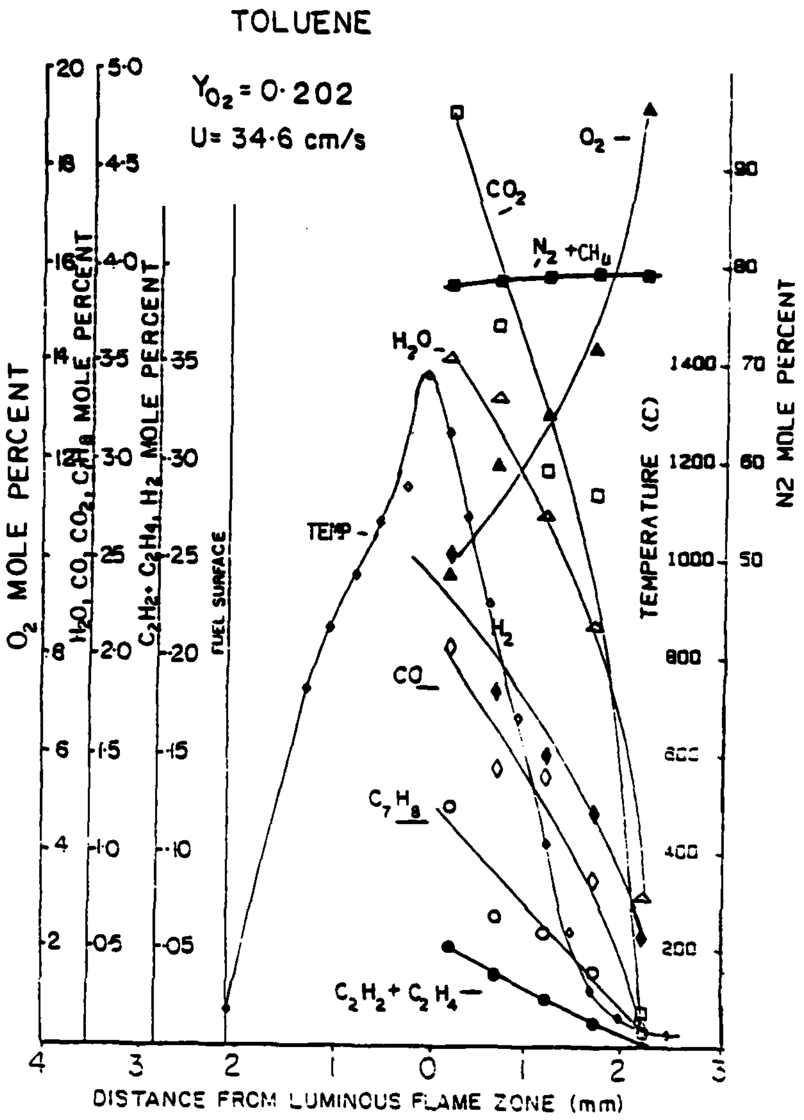

FIGURE 2

Composition profiles of stable species and temperature profile in a diffusion flame above a burning pool of toluene.

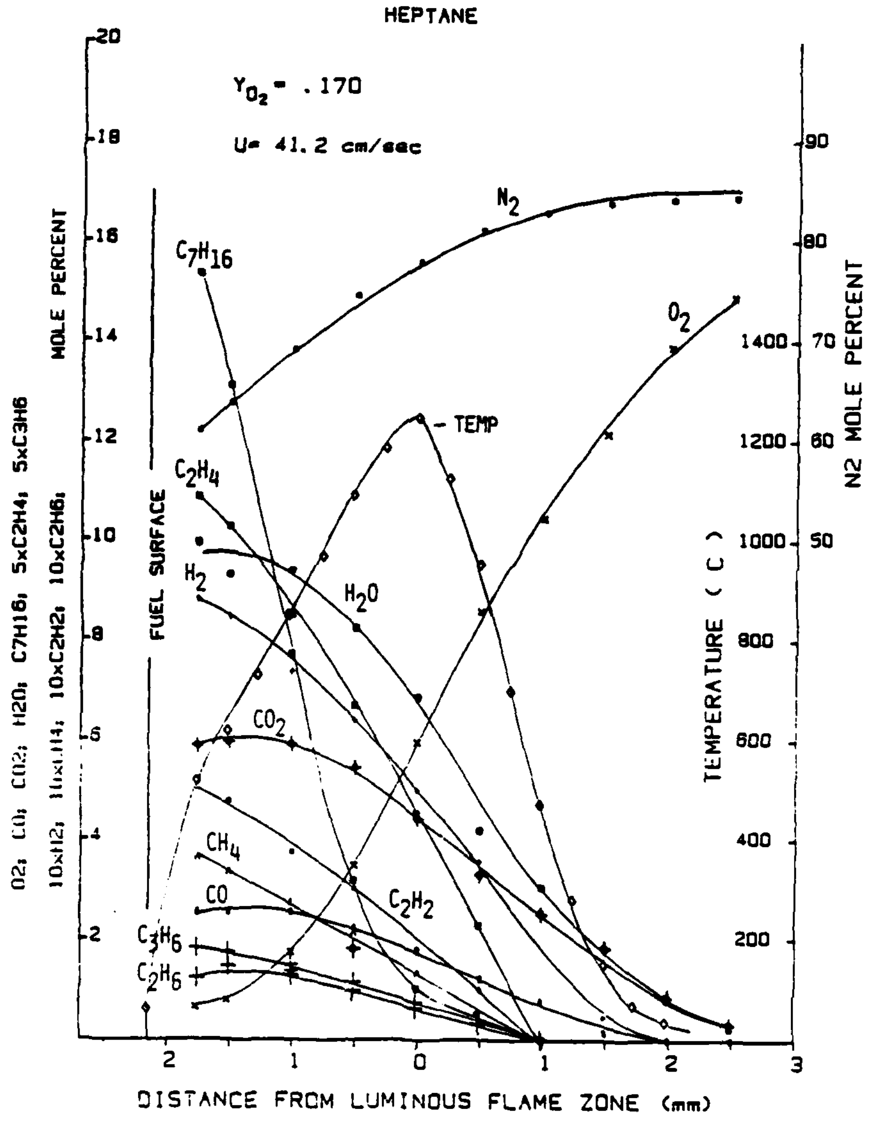

FIGURE 3

Composition profiles of stable species and temperature profile in a diffusion flame above a burning pool of heptane.

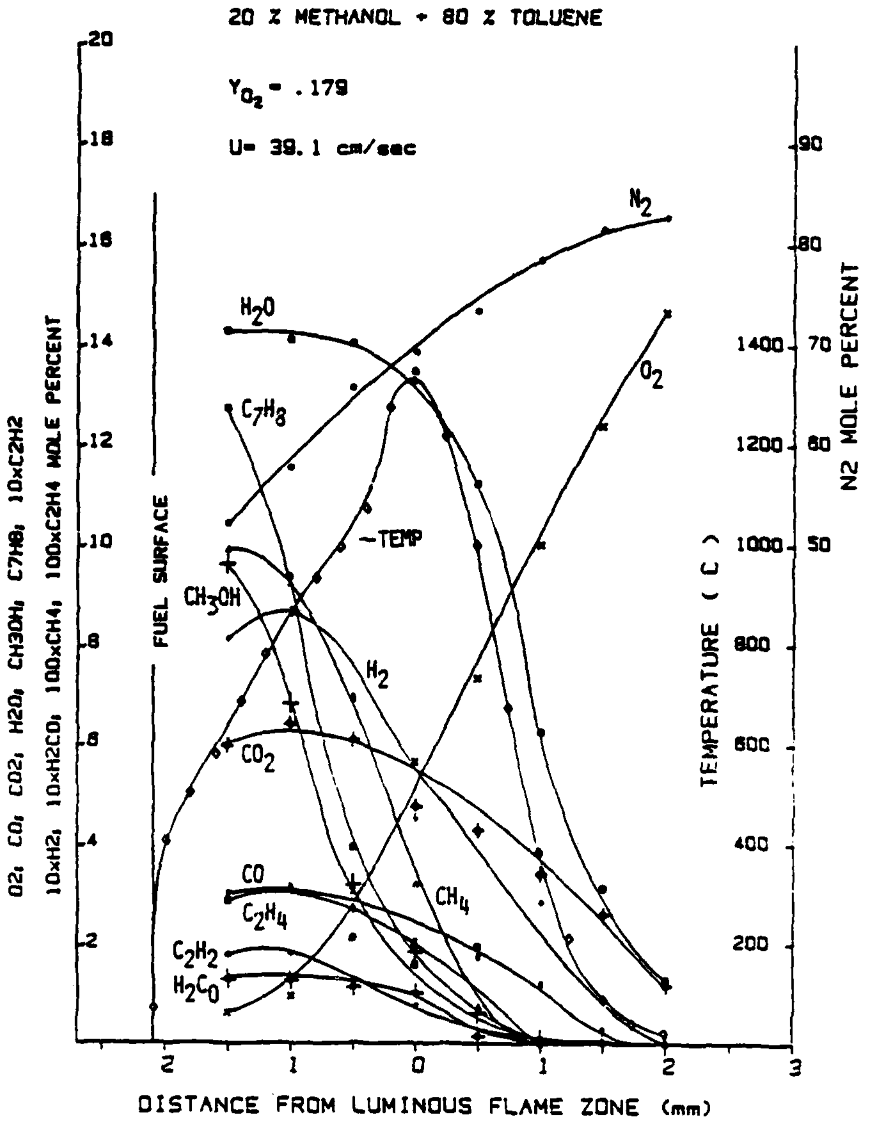

FIGURE 4

Composition profiles of stable species and temperature profile in a diffusion flame above a burning pool of a solution of 20% methanol and 80% toluene by volume.

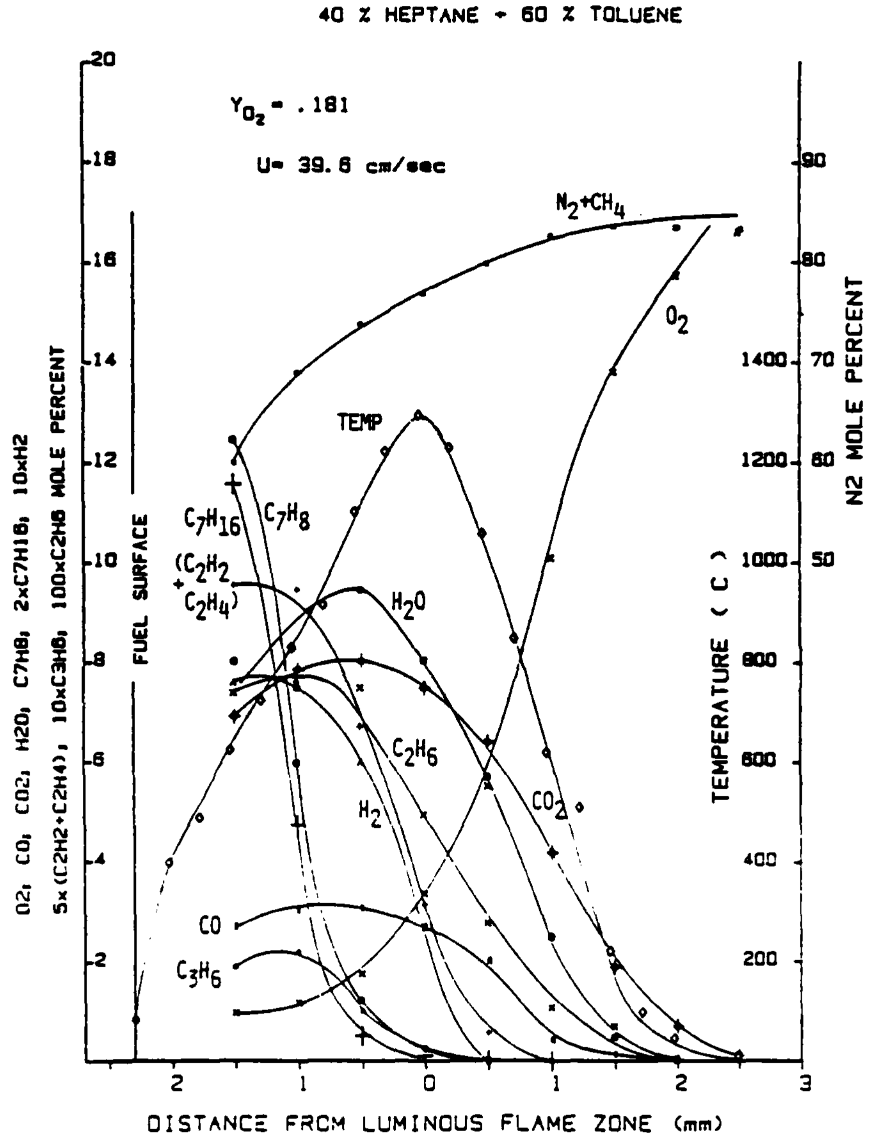

FIGURE 5

Composition profiles of stable species and temperature profile in a diffusion flame above a burning pool of a solution of 40% heptane and 60% toluene by volume.

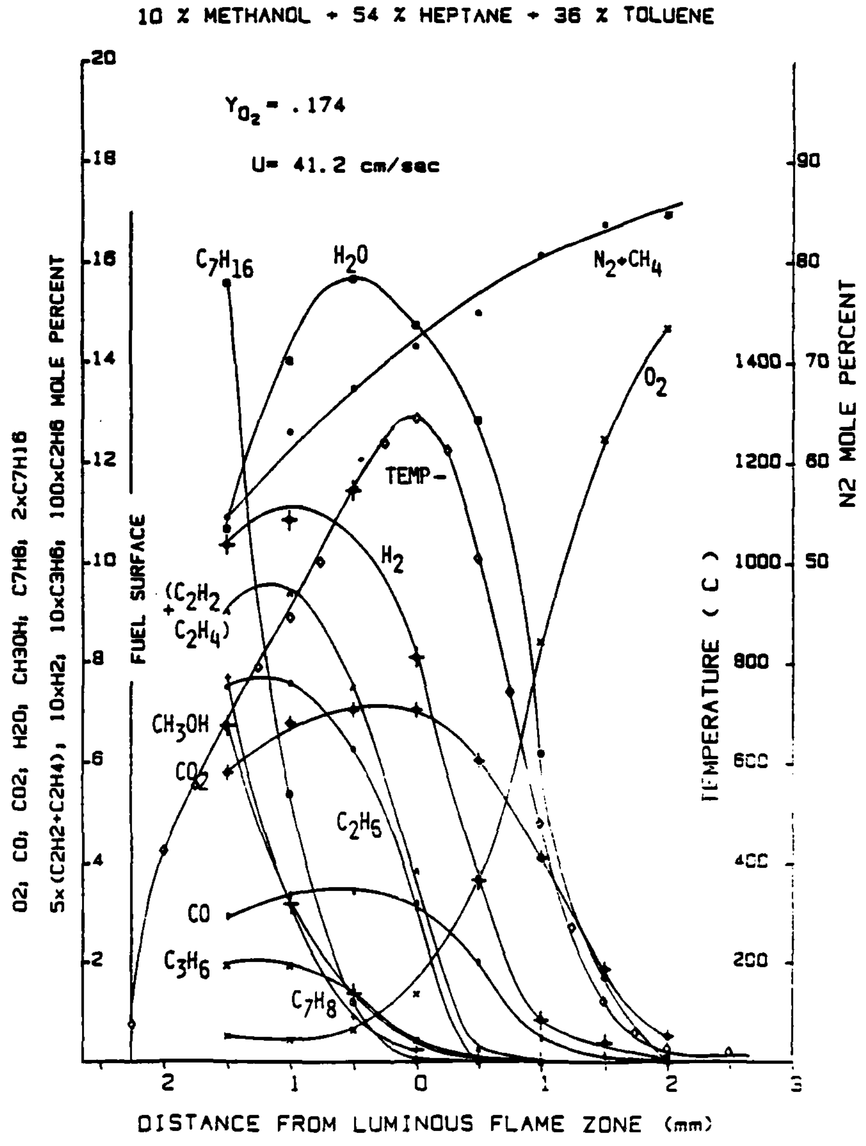

FIGURE 6

Composition profiles of stable species and temperature profile in a diffusion flame above a burning pool of a solution of 10% methanol, 54% heptane, and 36% toluene by volume.

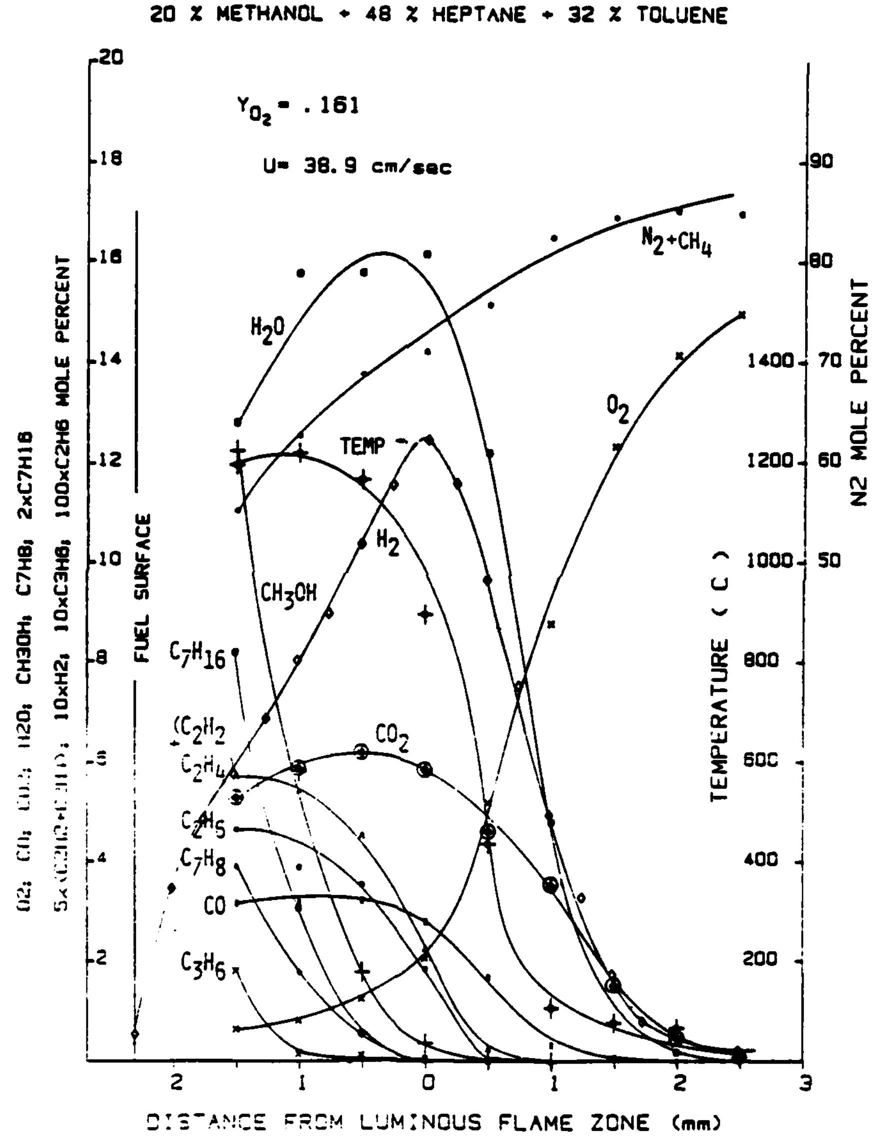

FIGURE 7

Composition profiles of stable species and temperature profile in a diffusion flame above a burning pool of a solution of 20% methanol, 48% heptane, and 32% toluene by volume.

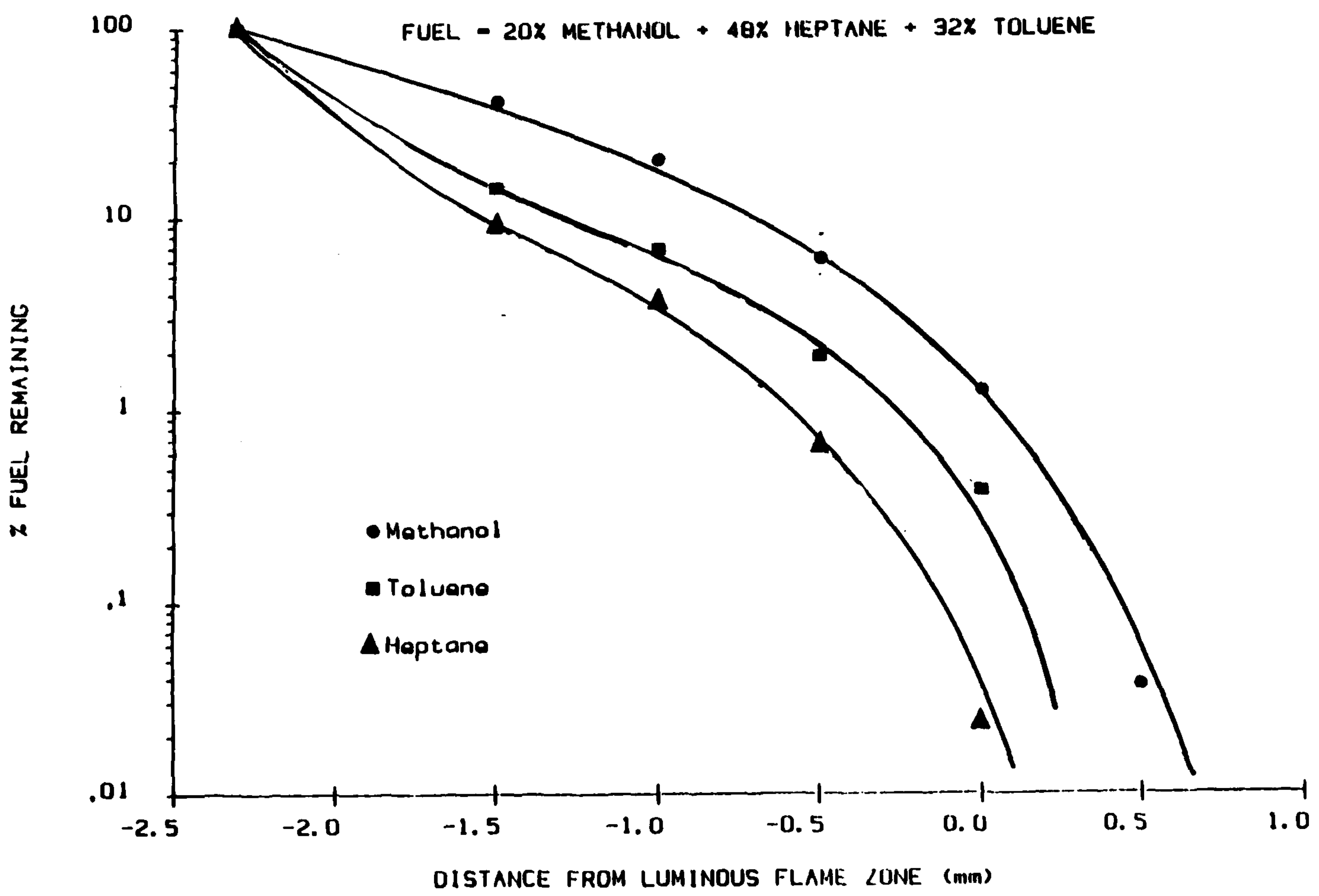

FIGURE 8

Concentration of fuels as a function of location in a diffusion flame burning a solution of 20% methanol, 48% heptane and 32% toluene by volume.

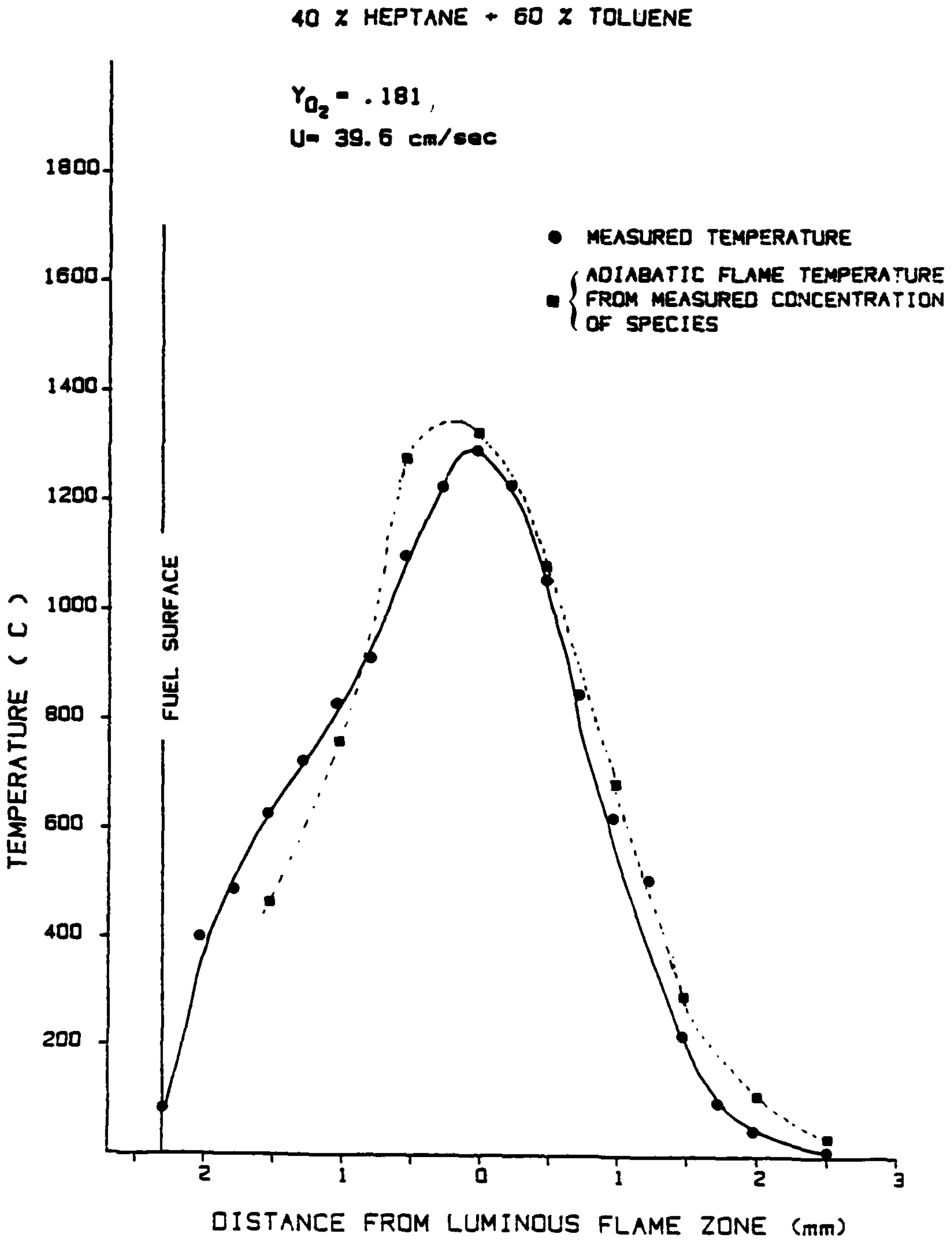

FIGURE 9

Measured temperature profile vs. that calculated from measured local composition of species for a fuel blend containing 40% heptane and 60% toluene by volume.

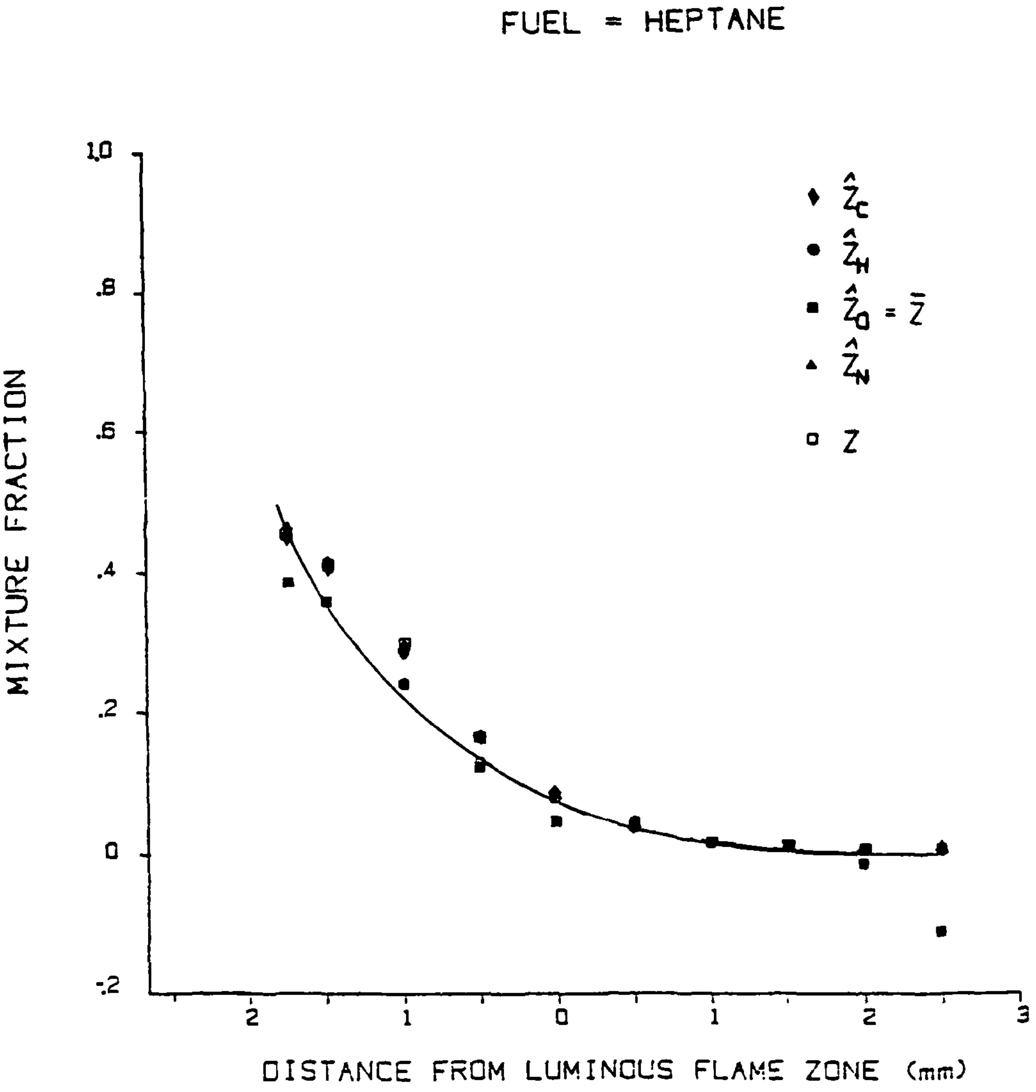

FIGURE 10

Various definition of mixture fractions namely Z, $\bar{Z}$, $\hat{Z}_C$ and $\hat{Z}_H$ as a function location for a diffusion flame burning heptane, with the same data as shown in Fig. 3.

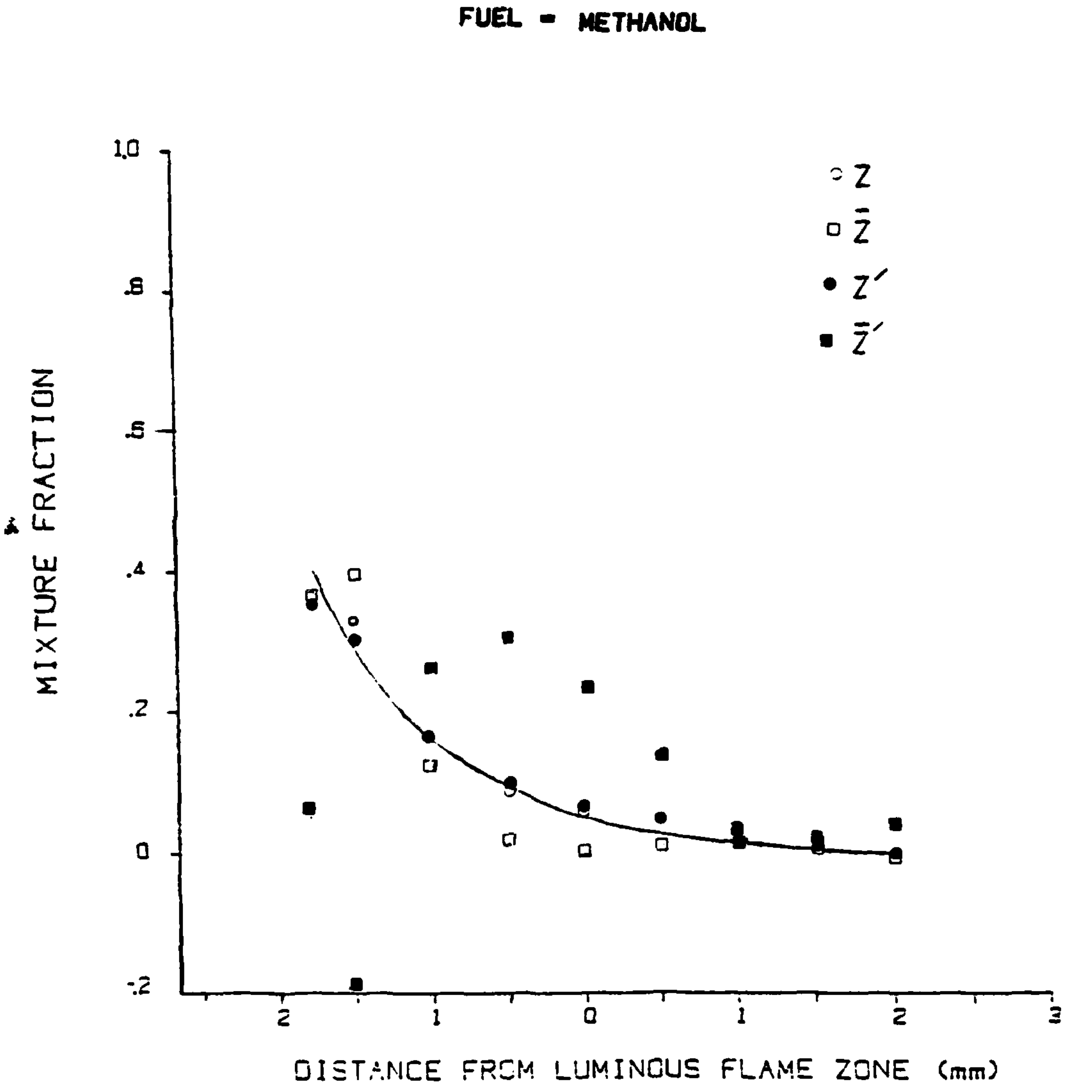

FIGURE 11

Plot of Z, Z', $\bar{Z}$ and $\bar{Z}'$ as a function of location for a diffusion flame burning methanol, with the same data as shown in Fig. 1.

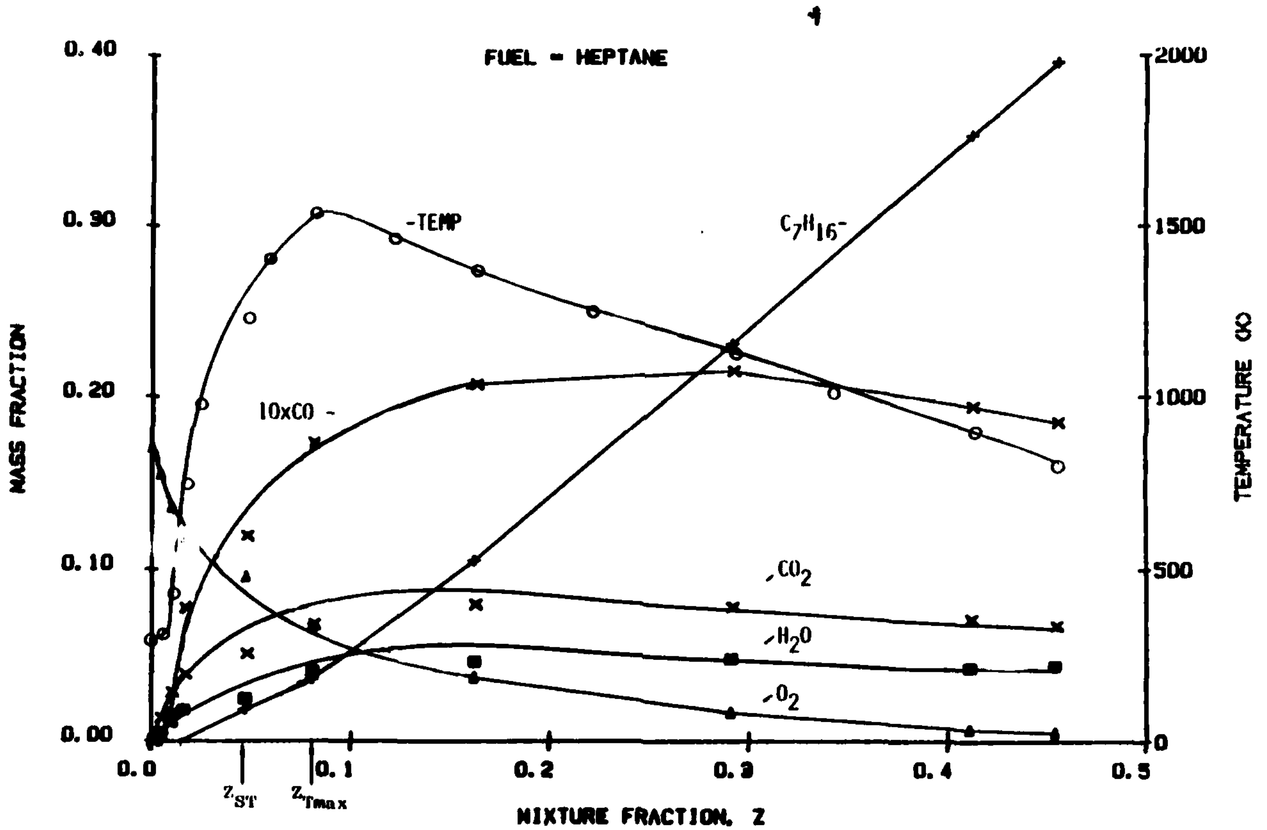

FIGURE 12

Composition profiles of major stable species in terms of mass fractions and temperature profile in a diffusion flame above a burning pool of heptane plotted with Z as the independent variable.

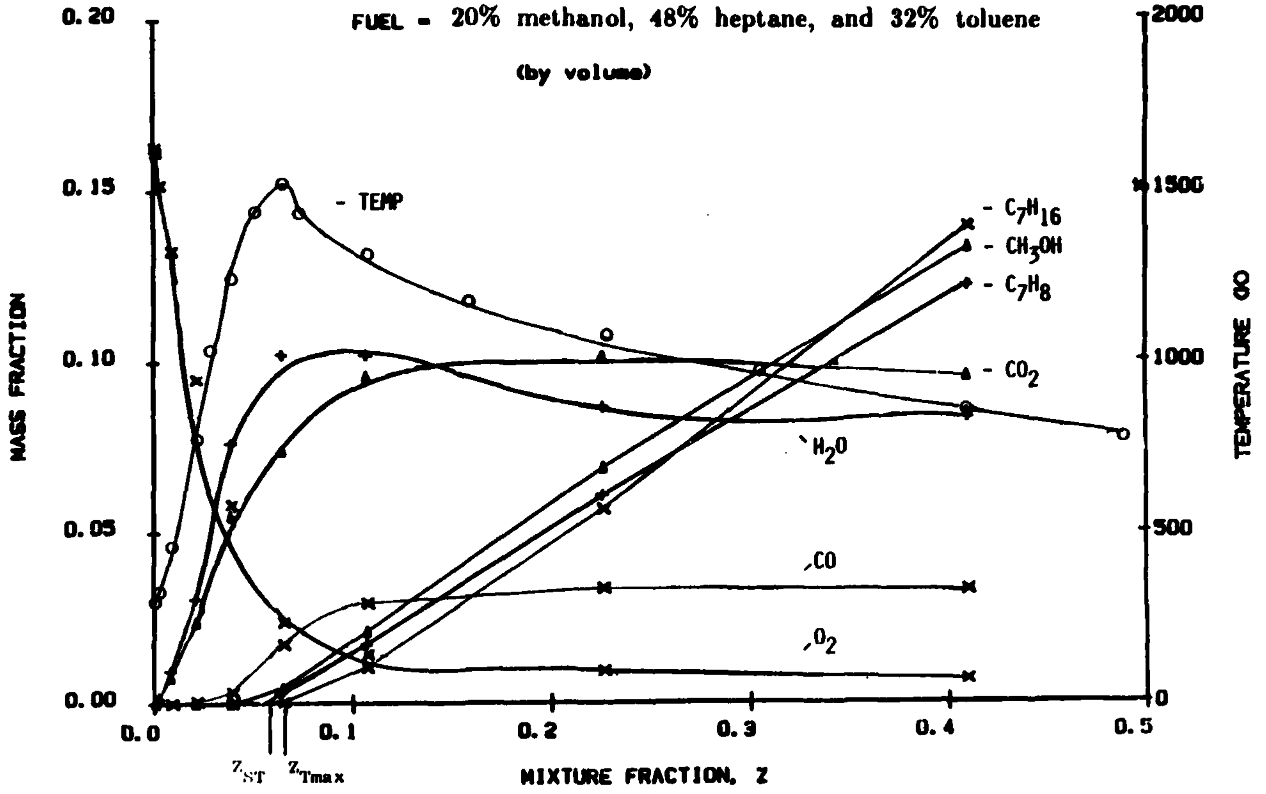

FIGURE 13

Composition profiles of major stable species in terms of mass fractions and temperature profile in a diffusion flame above a burning pool of a solution of 20% methanol, 48% heptane and 32% toluene by volume plotted with Z as the independent variable.

CHAPTER VII

STRUCTURE AND EXTINCTION OF A COUNTERFLOW PARTIALLY PREMIXED, DIFFUSION FLAME

ABSTRACT

The fundamental heat and mass transport processes in a partially premixed, diffusion flame stabilized between counterflowing streams of fuel A, and fuel B premixed with an oxidizer C and an inert gas are analyzed. The gas phase chemical reaction between fuel A and the oxidizer C and between fuel B and the oxidizer C is approximated as a one step process. Asymptotic analysis is performed in the limit of a large value for the ratio of the activation energy characterizing the chemical reactions to the thermal energy in the flame. Guided by experimental results it is presumed that two distinct, thin reaction zones are present, a premixed flame and a diffusion flame. The outer structure and the inner structure of the reaction zones are analyzed. It is shown that for the flame to extinguish the reaction zones must merge. The outer structure and inner structure of the merged reaction zone is analyzed. An explicit algebraic relation is obtained relating the Damköhler number at extinction to the ambient conditions in the counterflowing streams, thermophysical properties of the reactants, and the overall chemical kinetic rate parameters characterizing the gas phase oxidation of the fuels.

The results of the analysis are then extended to a merged flame that is stabilized in a stagnation point boundary layer over the surface of a liquid fuel when a premixed stream of gaseous fuel and oxidizer flows over its surface. To test the predictions of the theory, extinction experiments are performed on a partially premixed, diffusion flame stabilized between a vaporizing surface of heptane and a gaseous stream consisting of methane, oxygen and nitrogen. It is observed that the stability of diffusion flames with an oxidizer stream premixed with fuel is

enhanced. This may be due to a combination of thermal and kinetic effects. The results are used to deduce the overall chemical kinetic rate parameters characterizing the gas phase oxidation of methane in a premixed flame and comparison is made with the results from other studies.

A detailed description of the research summarized above has been published in Chemical Engineering Science 40, No. 1, 2027-2038, 1985. The authors of the publication were Dr. A. P. Hamins, Mr. H. Thridandam and Dr. K. Seshadri.

CHAPTER VIII

THE STRUCTURE OF COFLOWING, LAMINAR DIFFUSION FLAMES BURNING DILUTED ETHANE, DILUTED ETHYLENE AND DILUTED ACETYLENE IN AIR

ABSTRACT

An experimental study of the chemical kinetic processes which lead to soot formation in laminar, coflowing, diffusion flames burning C_2 hydrocarbon fuels is outlined here. The fuels studied were ethane, ethylene, and acetylene. The measurements made were composition profiles of a number of stable species in these flames which were obtained by use of gas sampling with quartz microprobes and gas chromatographic analysis. Temperature measurements were made by use of Pt-Pt 10%Rh thermocouples. Each of the fuels was diluted with sufficient nitrogen and the fuel velocity was adjusted such that flames two cm in height were established. Experimental results are discussed in terms of chemical mechanisms of soot formation.

The ratio of benzene to acetylene was experimentally measured to be lowest in the case of the acetylene flame, which has the highest propensity to soot of all of the fuels tested. Consequently, it is suggested that benzene does not play a direct role in soot production. In addition, it was observed that 1.3 Butadiene is not present in acetylene flames indicating that this compound is not a direct intermediate to soot formation. A consideration of the concentration profiles of hydrogen in these three flames suggests that a reaction between young soot particles and acetylene occurs.

1. INTRODUCTION

A number of theoretical and experimental studies on the chemical kinetic mechanisms of soot formation in laminar diffusion flames have been reported (Glassman and Yaccarino, 1981, 1980, Kent *et al.*, 1981, Saito, 1983, Saito *et al.* 1985a, 1985b). These studies have attempted to identify species that act as precursors to soot formation in laminar diffusion flames. It has been suggested that compounds such as benzene, toluene, acetylene (Porter, 1953), butadiene, as well as ions (Olson and Calcote, 1981) are responsible for the formation of soot during combustion. Although a number of chemical kinetic mechanisms for soot formation have been postulated, the complexity of the problem has caused a full understanding of the processes involved to remain unclear. The results of experimental measurements on overventilated coflow, diffusion flames burning ethane, ethylene, and acetylene in air are reported below. Experimental results are discussed in terms of the chemical mechanisms leading to soot formation.

Glassman and Yaccarino, (1981) have shown from studies on diffusion flames that acetylene forms soot more readily than ethylene and that ethylene forms soot more readily than ethane. The differences in rates of soot production among these fuels is clearly dependent on the chemical kinetic mechanisms of fuel pyrolysis. Therefore, a comparison of the structure of diffusion flames burning these fuels can help in identifying compounds responsible for soot production. In addition, by studying flames which have only a small portion of their volume which contains soot particles, it is hoped that attention can be focussed on the chemical processes which are responsible for the formation of soot. In this paper we report on such results.

To facilitate meaningful interpretation of the experimental results it is necessary to have a rational basis for comparing the structure of diffusion flames. Saito (1983) observed that at a critical value of the flow rate of the fuel and at a critical value of the concentration of the fuel an orange region appeared at the tip of an overventilated, diffusion flame. This phenomena was observed for a number of gaseous hydrocarbon fuels (Saito *et al.* 1985a), specifically for CH_4, C_2H_6, C_3H_8, $n-C_4H_{10}$, C_2H_4, C_3H_6, C_4H_8, C_4H_6 and C_2H_2. Saito *et al.* (1985a) have suggested that the orange region corresponds to radiant emission from the soot particles whose temperature are in equilibrium with those of the gas. However, in the yellow region the temperature of the soot particles is higher than that of the gas due to energy release associated with carbon particle growth by polymerization of olefinic or aromatic species on the surface of the soot particle. Saito *et al.* (1985a) also observed that in the yellow region of a diffusion flame near the orange zone the concentration of olefins dropped rapidly. In addition, it was observed that the temperature at the tip of a diffusion flame with a tiny orange region is very similar for a wide range of hydrocarbon fuels including C_2H_6, C_2H_4, and C_2H_2 (Saito *et al.*, 1985a). These observations suggest that if a comparison is made of the structure of diffusion flames burning C_2 hydrocarbon fuels under the condition where an orange region just appears on the tip, the evolution of soot particles and other intermediate compounds would be similar. In addition, if the flame heights are the same, then the residence times of the various compounds in the diffusion flame would be similar (Saito *et al.*, 1985a).

An experimental investigation concerning the chemical kinetic processes which occur in diffusion flames burning C_2 hydrocarbon fuels is outlined here. Composition profiles of a number of stable species were measured in these flames by use of gas sampling with quartz microprobes and gas chromatographic analysis. Temperature measurements were made by use of Pt-Pt 10%Rh thermocouples. In Section 2 the experimental apparatus and procedure for making the measurements is described. The results are interpreted in Section 3. Conclusions are summarized in Section 4.

2. APPARATUS

The coflow burner assembly is described in Chapter II. Fuel mixed with nitrogen was introduced into the inner tube and synthetic air from the outer tube. The velocity of air in the outer concentric tube was maintained at a constant value equal to 2 cm/sec. Initially the fuel flow rate was adjusted such that a diffusion flame approximately 2 cm in height was stabilized in the burner. Nitrogen was gradually added to the fuel stream and the fuel flow rate was adjusted simultaneously such that one could stabilize a diffusion flame 2 cm in height with a small orange zone at the flame tip. Figure 1 shows a sketch of a diffusion flame with an orange tip.

The fuels used were ethane (99.0% purity), ethylene (99.5% purity) and acetylene (99.6% purity). The composition of the synthetic air was measured to be 21% oxygen and 79% nitrogen. Commercially available acetylene is often mixed with acetone for purposes of safety. The concentration of acetone vapor in acetylene has been measured to vary from 1% to 20% depending on the pressure of acetylene in the cylinder. Therefore, acetylene was purified by use of a three stage filtering process as described in Section B of this chapter before introducing this compound into the burner. Table 1 shows conditions at which diffusion flames two cm in height with a small orange zone at the tip were stabilized in our burner. Table 1 indicates that the ratio of the concentration of fuel to that of nitrogen is the highest for C_2H_6 followed by C_2H_4 and C_2H_2. This result is consistent with the observations of Saito *et al.* (1985a). The conditions at which the orange region appeared were weakly dependent on the velocity of the oxidizing gas stream consistent with the previous observation of Saito *et al.* (1985a).

Composition profiles were measured by use of quartz microprobes. A description of the sampling system, gas chromatograph, and the experimental procedure is given in detail in Chapter II. The location of the tip of the probe with reference to the edge of the fuel duct was determined by use of a cathetometer, having a reading accuracy of 0.005 mm. As the probe was not heated, condensation of water vapor occurred in the probe, therefore the profiles of water vapor are not reported. The results of concentration profiles on a dry basis are sufficient for drawing the general conclusions discussed here. Samples were withdrawn from the flame at a line pressure of 725 torr. Sampling at a lower pressure was observed to cause distortion of the flame. A sampling time of six minutes was estimated to be sufficient to fill the sampling loop of the GC with a representative sample from the flame. After completing a run, the condensed water and deposits of soot in the microprobe were dispelled by temporarily heating the probe externally with a bunsen burner, and removing the products by use of a vacuum pump.

The concentration of stable species was measured at a number of points in the axial direction. Data for diffusion flames burning ethane, ethylene, and acetylene are shown in Figs. 2-7. The data shown in Figs. 6 and 7 were obtained after removing the acetone impurity from acetylene (see section B of this chapter). Due to a large number of species detected two figures are shown for each fuel, profiles of the major species are shown in Figs. 2, 4, and 6, while profiles of the trace species are shown in Figs. 3, 5, and 7. The temperature profiles shown in Figs. 2, 4, and 6 were measured by using Pt-Pt 10% rhodium thermocouples of 0.0508 mm wire diameter. The thermocouples were coated with a layer of SiO_2 to prevent catalytic heating effects. Corrections for radiant heat losses from the thermocouple bead were made by use of a method described by Seshadri and Rosner (1981). In the yellow regions of the flame there was deposition of soot on the thermocouple bead. Therefore, data was obtained during a certain interval and the result was extrapolated to the time of insertion of the thermocouple into the flame (Saito *et al.*, 1985b).

3. DISCUSSION OF EXPERIMENTAL RESULTS

Figures 2, 4, and 6 show that in these C2 hydrocarbon flames, the concentration of fuel decreases rapidly in the axial direction until nearly all of the fuel is consumed near the flame sheet. These figures also show that the concentration of oxygen initially decreases along the axial direction measured from the base of the burner, reaches a minimum value and increases dramatically towards the flame front. At the cold burner lip, liftoff of the flame allows O_2 to leak into the fuel rich region from the sides. This O_2 is subsequently burnt as the temperature increases axially until a point is reached where the concentration of O_2 increases due to penetration through the flame sheet. These profiles suggest that O_2 consumption actually occurs even below the yellow sooting zone of these flames. Figs. 2-7 also show that oxygen is always very small in the flame cone. The profiles are similar to those which have been reported by Saito *et al.* (1985b) for non-diluted methane diffusion flames. Figures 2-7 show that the concentration of olefins approaches zero before the onset of the orange zone as has been reported previously for methane flames (Saito *et al.*, 1985b).

The profiles of temperature in Figs. 2, 4, and 6 show that the maximum temperature in these flames differ by about 100 ℃, yet the temperature at the onset of the orange regions are similar in value and are 1634 ℃, 1646 ℃, and 1589 ℃ respectively for the ethane, ethylene, and acetylene flames. Saito *et al.* (1985a) obtained values of 1375 ℃, 1370 ℃, and 1350 ℃ respectively for the temperature at the tip of a flame with a tiny orange region in non-diluted ethane, ethylene, and acetylene coflowing diffusion flames. These temperatures (Saito *et al.*, 1985a) were not corrected for radiative losses from the thermocouple bead. However, when their estimate for radiative losses of 200 ℃ (Saito *et al.*, 1985a) is used to modify their temperature data, good agreement is achieved between their results and ours.

Figure 2 shows that the major intermediates formed from pyrolysis of the ethane flame, in order of their concentrations are H_2, C_2H_4, C_2H_2, and CH_4. A possible pyrolysis mechanism can be postulated as follows (Back, 1972):

$$C_2H_6 + M \rightarrow 2\ CH_3 + M \tag{1}$$

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \tag{2}$$

$$C_2H_5 + M \rightarrow C_2H_4 + H + M \tag{3}$$

$$C_2H_6 + H \rightarrow H_2 + C_2H_5 \tag{4}$$

Ethane decomposition leads to C_2H_4 production as outlined in reactions (1)-(4). Ethylene pyrolysis is described in reactions (6)-(8) below.

Figure 4 shows that the major decomposition products formed during pyrolysis of ethylene are C_2H_2 and H_2. The essential path in ethylene decomposition may be postulated to occur via the following series of bimolecular reactions (Back *et al.*, 1972):

$$C_2H_4 + C_2H_4 \rightarrow C_2H_5 + C_2H_3 \tag{5}$$

$$C_2H_3 + M \rightarrow C_2H_2 + H + M \tag{6}$$

$$C_2H_4 + H \rightarrow C_2H_3 + H_2 \tag{7}$$

Other studies utilizing shock tube techniques (Just *et al.*, 1976) indicate that a more important decomposition during pyrolysis of ethylene at high temperatures may be the following reaction, where ethylene pyrolyzes directly to form acetylene and hydrogen.

$$C_2H_4 + M \rightarrow C_2H_2 + H_2 + M \tag{8}$$

In either scheme, the major stable products of pyrolysis of ethylene are C_2H_2 and H_2 as seen in Fig. 4.

Figures 2 and 4 show that pyrolysis of ethane and ethylene lead to a rapid production of acetylene. In general, it can be concluded that the chemical decomposition of both ethylene and ethane proceeds via acetylene. Thus, the pyrolysis of acetylene can be considered to have the simplest chemistry of the three C2 hydrocarbon flames investigated.

The pyrolysis of acetylene has been studied by a large number of experimenters at low temperatures and in shock tubes. The pyrolysis products of acetylene vary depending on the temperature environment. Figure 6 shows that H_2 was observed to be the pyrolysis product with the largest concentration. A possible mechanism for the pyrolysis of acetylene has been suggested by Back (1972) as:

$$C_2H_2 + C_2H_2 \rightarrow C_2H_3 + C_2H \tag{9}$$

$$C_2H_3 + C_2H_2 \rightarrow C_4H_5 \tag{10}$$

$$C_4H_5 \rightarrow C_4H_4 + H \tag{11}$$

$$C_2H + C_2H_2 \rightarrow C_4H_3 \tag{12}$$

$$C_4H_3 \rightarrow C_4H_2 + H \tag{13}$$

Furthermore, it has been suggested that polyacetydes, which may be soot precursors, can be formed during reaction of the C_2H radical as in the following steps (Tanzawa and Gardiner, 1978).

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \tag{14}$$

$$C_4H_2 + C_2H \rightarrow C_6H_2 + H \tag{15}$$

Another possible route to soot formation is via acetylene, which can form a polymer which can then dehydrogenate to form young soot particles. It has been shown that young soot particles grow rapidly by a gas phase - solid phase set of reactions (Cullis, 1966, and Schmieder, 1982).

Figures 2, 4, and 6 shows that the concentration of intermediate species such as CH_4 increases in the axial direction when measured from the burner duct, reaches a maximum value and begins to decrease towards the flame front. The concentration of CH_4 and H_2 in the ethane flame (Fig. 2) is larger than that in the ethylene flame (Fig. 4), which in turn is larger than that in the acetylene flame (Fig. 6). The concentration of CH_4 attains its maximum value at just about the same axial location in the ethylene flame (Fig. 4) and the acetylene flame (Fig. 6), while the maximum value of the concentration of CH_4 in the ethane flame is closer to the fuel duct (Fig. 2). The pyrolysis pathway in ethane decomposition leads directly to CH_4 production *as seen in reaction (2) and accounts for the location and relatively large* value of the maximum CH_4 concentration when compared to the other C2 flames.

As H_2 has a relatively large diffusion coefficient and is relatively stable at high temperatures, its profile must represent a balance between the rate of formation of H_2 by pyrolysis, transport by convection and diffusion, and consumption at the flame sheet. Figures 2 and 4 show that the maximum concentration of H_2 in the ethane flame occurs much closer to the burner duct when compared to the H_2 peak in the ethylene flame. This reflects the very rapid dehydrogenation rate of ethane to C_2H_2 when compared to ethylene. The H_2 profile in the acetylene flame (see Fig. 6), however, does not obtain a maximum value even in the yellow region of the flame, indicating very rapid dehydrogenation late in the flame, just before the flame sheet where H_2 is consumed. This observation confirms the work of previous studies which suggest that a rapid buildup of soot may occur as:

$$\text{Soot} + C_2H_2 \rightarrow \text{Soot(increase)} + H_2 \qquad (16)$$

Acetylene dehydrogenation in the yellow sooting region of the ethane and ethylene flames is masked due to the large amount of H_2 available from the pyrolysis of C_2H_6 and C_2H_4 earlier in the flame.

The maximum percentage of C_3H_6 in the ethane flame is about a factor of four larger than in the ethylene flame and about a factor of 30 larger than in the acetylene flame. Furthermore, the location of the maximum C_3H_6 peak flame closely follows the maximum value of C_2H_4 in the ethane flame. Comparing the ethane and ethylene flames at the h/H = .3 to about .45 region, the value of the C_2H_4 present is only a factor of 2 to 4 less in the ethane flame than in the ethylene flame, where H is defined as the flame height (about 20 mm in all cases) and h is the axial position in the flame measured from the burner duct. However the concentration of C_2H_6 is about a factor of 700 less in the ethylene flame than in the ethane flame near these locations. The large quantity of CH_4 in the ethane flame suggests that large concentrations of CH_3 are prescent. Gordon and McNesby (1959) suggested a mechanism for propylene production where a methyl radical reacts with ethylene to form a n-propyl radical:

$$CH_3 + C_2H_4 \rightarrow CH_3(CH_2)_2 \qquad (17)$$

This radical may then react with ethylene to form n-pentyl which isomerizes by intramolecular abstraction as in the following step:

$$CH_3(CH_2)_4 \rightarrow CH_3CH(CH_2)_2CH_3 \qquad (18)$$

This radical may then pyrolyze to propylene and an ethyl radical as in the following step:

$$CH_3CH(CH_2)_2CH_3 \rightarrow CH_3CHCH_2 + C_2H_5 \qquad (19)$$

Thus, the large quantity of CH_3 and C_2H_4 as pyrolysis intermediates in an ethane flame, would encourage C_3H_6 production.

Benzene was found to be a minor component in all of the flames, including the acetylene flame. Table 2 compares the ratio of the concentration of benzene to that of acetylene as a function of h/H. Data for methane was obtained from Saito *et al.* (1985b). This ratio obtains a maximum value between h/H=0.6 and 0.75 for all cases. For the undiluted methane fuel the ratio of benzene to acetylene increases as the absolute concentration of acetylene increases in the flame. This correlation, however, is not consistent when comparing the three C2 hydrocarbon flames. Table 2 shows that this ratio is largest for the ethane flame (Fig. 3) followed by the ethylene flame (Fig. 5) and the acetylene flame (Fig. 7). The ratio of benzene to acetylene is smallest for the pure C_2H_2 flame by about a factor of 4, where the concentration of acetylene is the lowest. The ratio is largest in the C_2H_6 flame where the concentration of acetylene is the lowest when compared with the other C2 flames. Since it has been established that in diffusion flames burning acetylene, soot forms more readily than in flames burning ethylene and that an ethylene diffusion flame forms soot more readily than an ethane flame, the results shown in Table 2 suggest that benzene is not a direct precursor to soot production, but instead may be a product of a secondary process. Table 2 also shows that the value of the ratio of the concentration of benzene to acetylene is larger by about a factor of 3 in the nonpurified acetylene flame (with one mole percent of acetone in the fuel) when compared to the purified acetylene flame. The data implies that free methyl radicals available from pyrolysis of acetone may enhance the production of a variety of intermediates such as benzene.

Table 3 shows results for the ratio of the concentration of certain intermediates in a nonpurified acetylene flame to that in a purified acetylene flame at two locations with h/H equal to 0.6, and 0.75. The acetone impurity in acetylene was measured to be 1 mole percent. Table 3 shows that while CH_4, C_3H_6, C_2H_6, allene, and methyl acetylene are enhanced by the presence of acetone, some intermediates such as H_2 are not affected. Clearly the results shown in Table 3 support the claim that the presence of acetone even in small quantities may have a significant effect on flame chemistry. Therefore, analysis of data obtained using unpurified commercial acetylene could be misleading.

It was observed that the same chemical species are present in all of these C2 flames (although in different quantities) as well as the methane flame of Saito *et al.* (1985c) with the notable exception of two intermediates which are missing from the acetylene flame. Figures 3, and 5 show that 1,3 butadiene and 1-Butene are present in ethane and ethylene flames with a maximum concentration of about 0.014% and .010% by mole respectively. However, the concentration of this compound was below the detectability limit of the GC (about 5 ppm) in the acetylene flame. Therefore, we conclude that 1,3 butadiene is not an important intermediate in the pyrolysis of acetylene. Furthermore, it has been suggested by Benson (1984) that butadiene is an important intermediate in the process of soot formation. Glassman has also suggested that butadiene or possibly the Butadienyl 1,3 radical is an important intermediate. The results presented in Fig. 7 negate the possibility that butadiene is important in soot formation in acetylene flames, although the butadienyl radical could play a role. However, if a small amount of acetone (1 mole percent) is burnt with the acetylene, 1,3 butadiene does appear and its peak concentration is of the order of 0.008 mole percent. Thus, there is evidence that the butadienyl radical may be present in the acetylene flame, but that the C-H bond in acetylene is so strong that it is a poor source of abstractable hydrogen. 1-Butene does not appear in the acetylene-acetone flame.

4. SUMMARY AND CONCLUSIONS

The temperature profiles and concentration profiles of stable chemical species in coflow diffusion flames burning ethane, ethylene, and acetylene was measured in order to obtain an improved understanding of the chemistry leading to soot formation. The fuels were diluted with nitrogen and the fuel flowrate was adjusted such that a flame 2 cm in height with a partly clear zone, a yellow sooting region and an orange tip was established. The following conclusions may be drawn from this study: The ratio of benzene to C_2H_2 was determined to be lowest in the case of the acetylene flame, which has the highest propensity to form soot of all of the fuels tested. Thus, it was confirmed that C_6H_6 probably does not play a direct role in soot production. The absence of 1,3 Butadiene in acetylene flames indicates that it also is not a direct intermediate in soot formation. A consideration of the profiles of hydrogen in these flames suggests the importance of the interaction between young soot particles and acetylene.

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FUEL COMPOSITION AND VELOCITY

FUEL TYPE	% N_2	% FUEL	VELOCITY (cm/sec)
PURE C_2H_2	89.2	10.8	1.55
C_2H_4	86.2	13.8	1.01
C_2H_6	78.6	20.9	0.605
NON-TREATED C_2H_2	89.2	10.8	1.55

TABLE 1

Composition and velocity of the fuel stream at which measurements were made. The velocity of the oxidizer stream was maintained at a constant value equal to 2 cm/sec.

RATIO OF BENZENE TO ACETYLENE

h/H FUEL	.15	.30	.45	.60	.75	.90
C_2H_2	0	.00003	.00106	.00268	.00334	.000662
C_2H_4	0	.00317	.00418	.0114	.0104	.00758
C_2H_6	0	.00463	.0123	.0150	.0148	.00329
NON-TREATED C_2H_2	-	-	-	.00379	.00879	-
CH_4a	.0055	.0135	.017	.024	.022	.0129
CH_4b	.0094	.022	.029	.033	.019	-

Note: all flames are 20 mm in height except CH_4a which was 14 mm.

TABLE 2

Ratio of the concentration of benzene to that of acetylene as a function of h/H along the axial direction for diffusion flames burning diluted ethane, ethylene and acetylene.

RATIO OF SPECIES IN NON-TREATED TO TREATED ACETYLENE FLAME

h/H SPECIES	0.6	0.75
H_2	1.0	1.1
CH_4	2.4	2.1
CO_2	1.1	1.0
C_2H_2	0.8	0.9
C_2H_4	1.7	3.2
C_2H_6	7.0	9.0
C_3H_6	3.7	3.6
PROPADIENE	1.6	2.7
METHYLACETYLENE	3.2	2.7
VINYLACETYLENE	1.0	1.1
DIACETYLENE	1.2	1.0
1,3 BUTADIENE*	.0008	.0002
C_6H_6	1.1	2.5

*Mole percentage in non-treated acetylene flame, (not present in treated flame).

TABLE 3

Ratio of the concentration of certain intermediate species in a purified acetylene flame to that in an acetylene flame with 1 mole percent of acetone contaminant in the fuel.

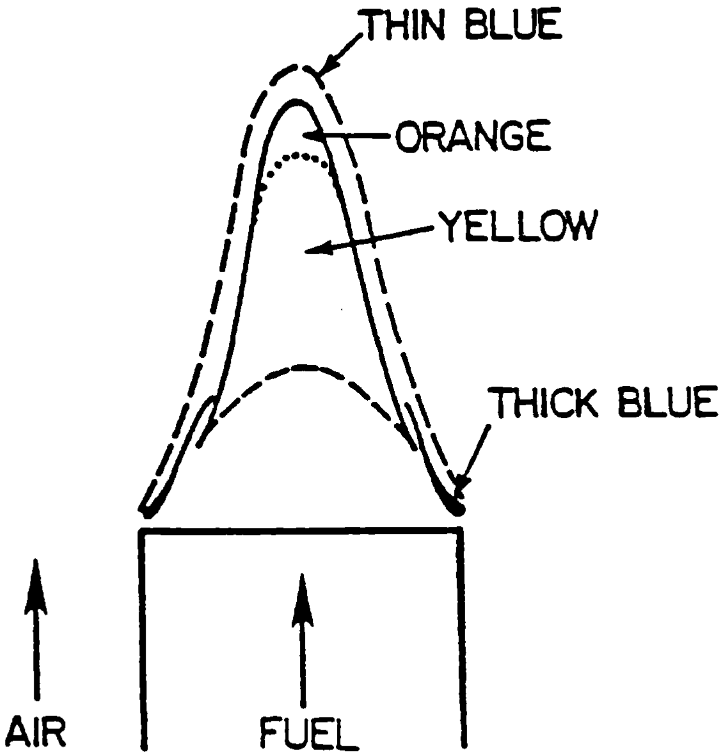

FIGURE 1

Schematic illustration of a typical diffusion flame showing the blue, yellow and orange zones, also see Figure 5 of Chapter II which shows a photograph of a coflowing ethylene diffusion flame with a small orange tip.

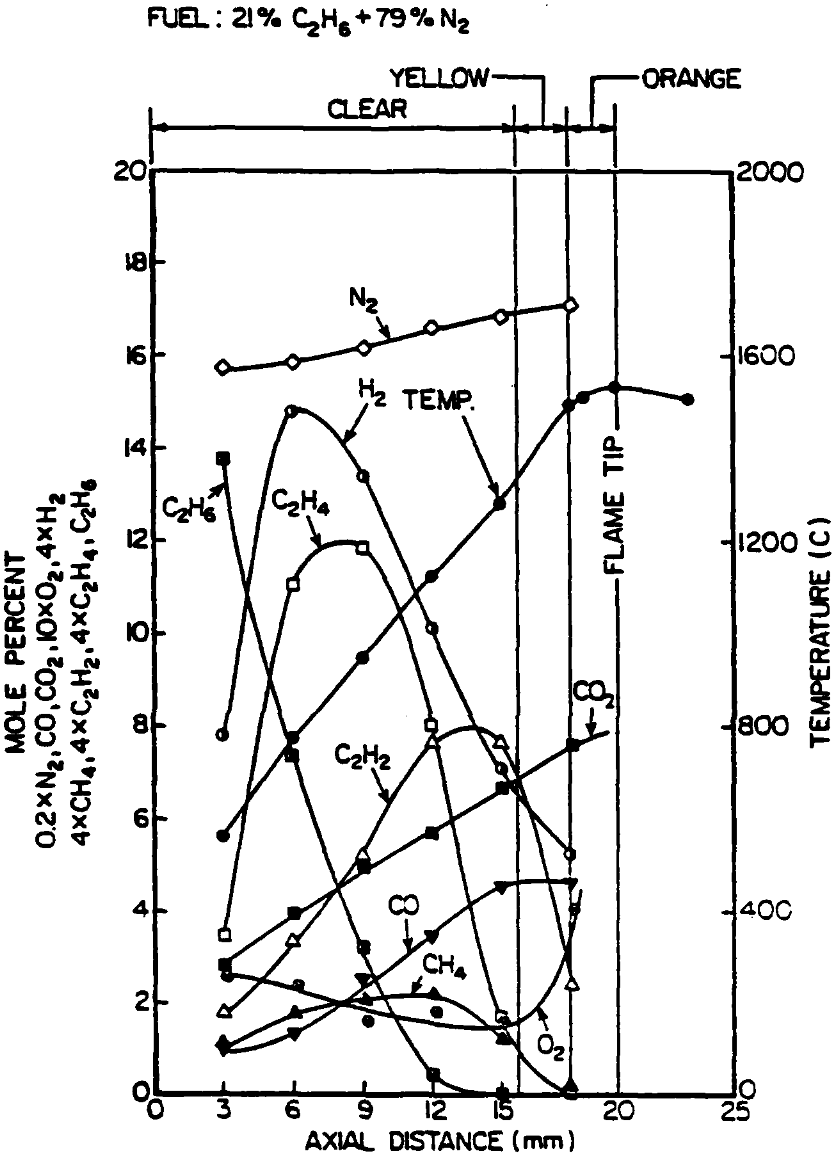

FIGURE 2

Axial profiles of concentration of major stable species in a laminar diffusion flame burning diluted ethane (20.9 mole percent) in air. The temperature profile is also shown.

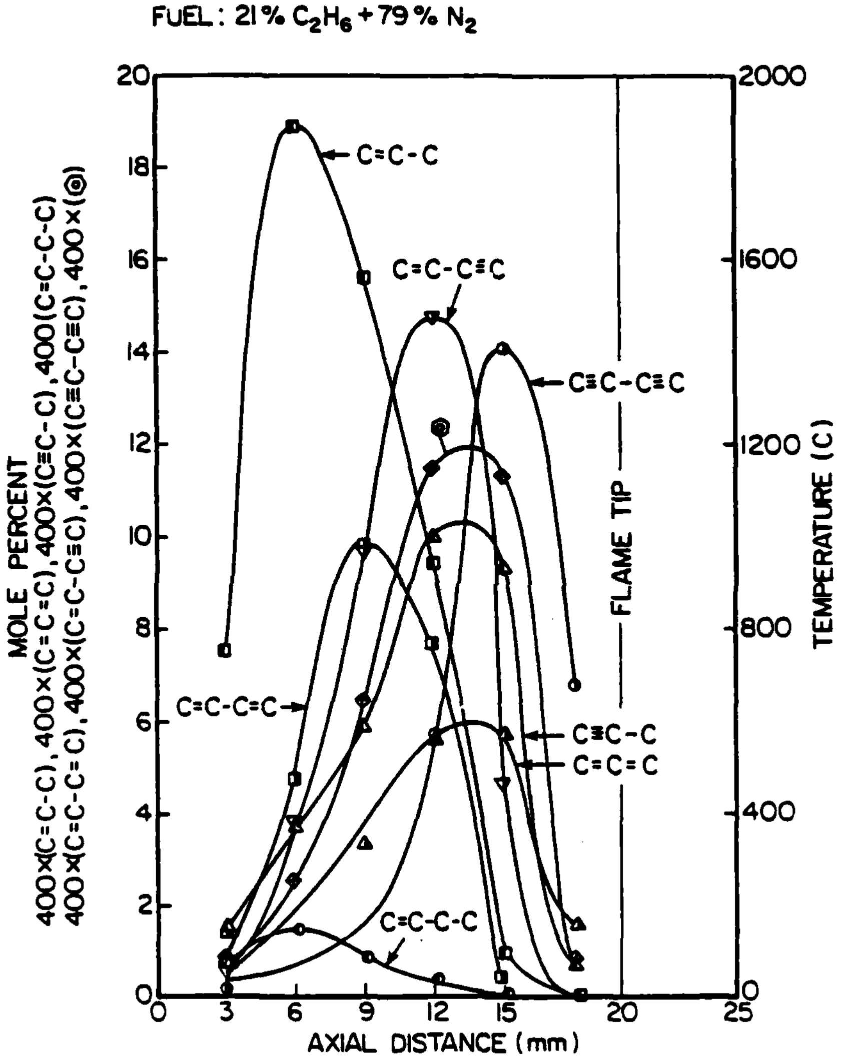

FIGURE 3

Axial profiles of concentration of trace species in a laminar diffusion flame burning diluted ethane (20.9 mole percent) in air.

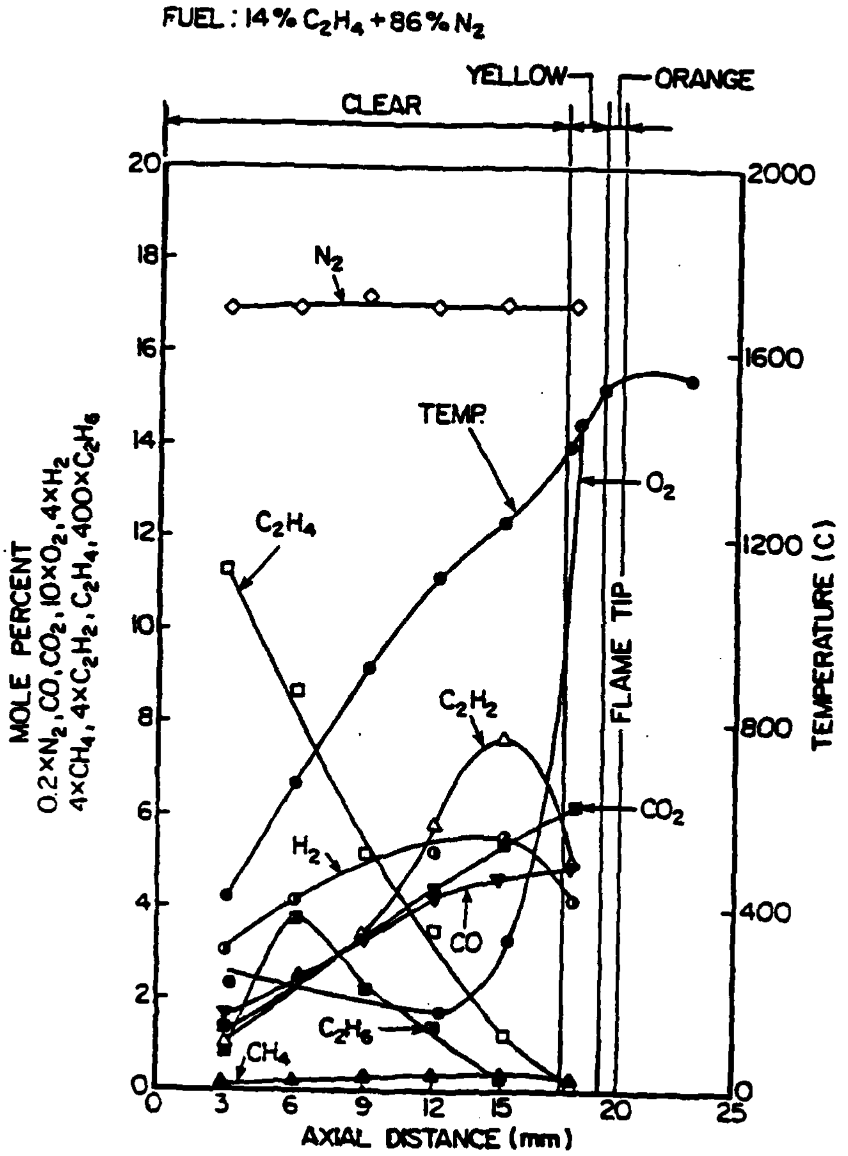

FIGURE 4

Axial profiles of concentration of major stable species in a laminar diffusion flame burning diluted ethylene (13.8 mole percent) in air. The temperature profile is also shown.

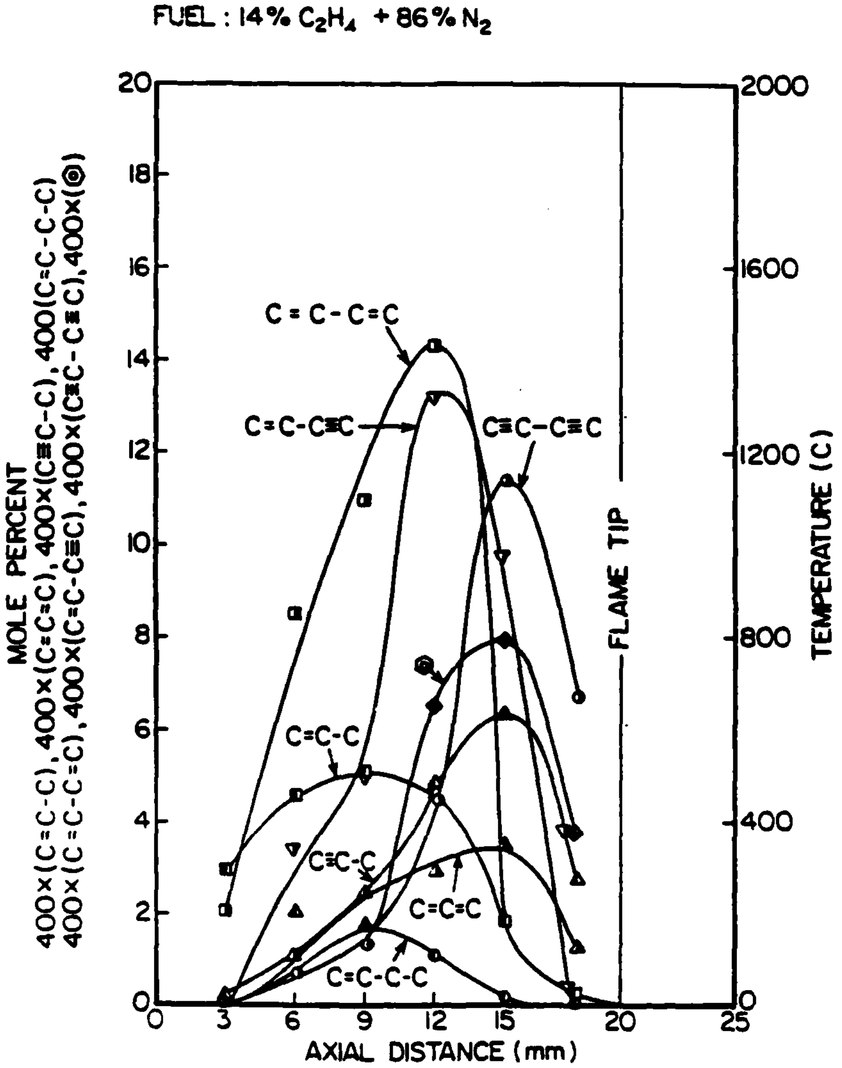

FIGURE 5

Axial profiles of concentration of trace species in a laminar diffusion flame burning diluted ethylene (13.8 mole percent) in air.

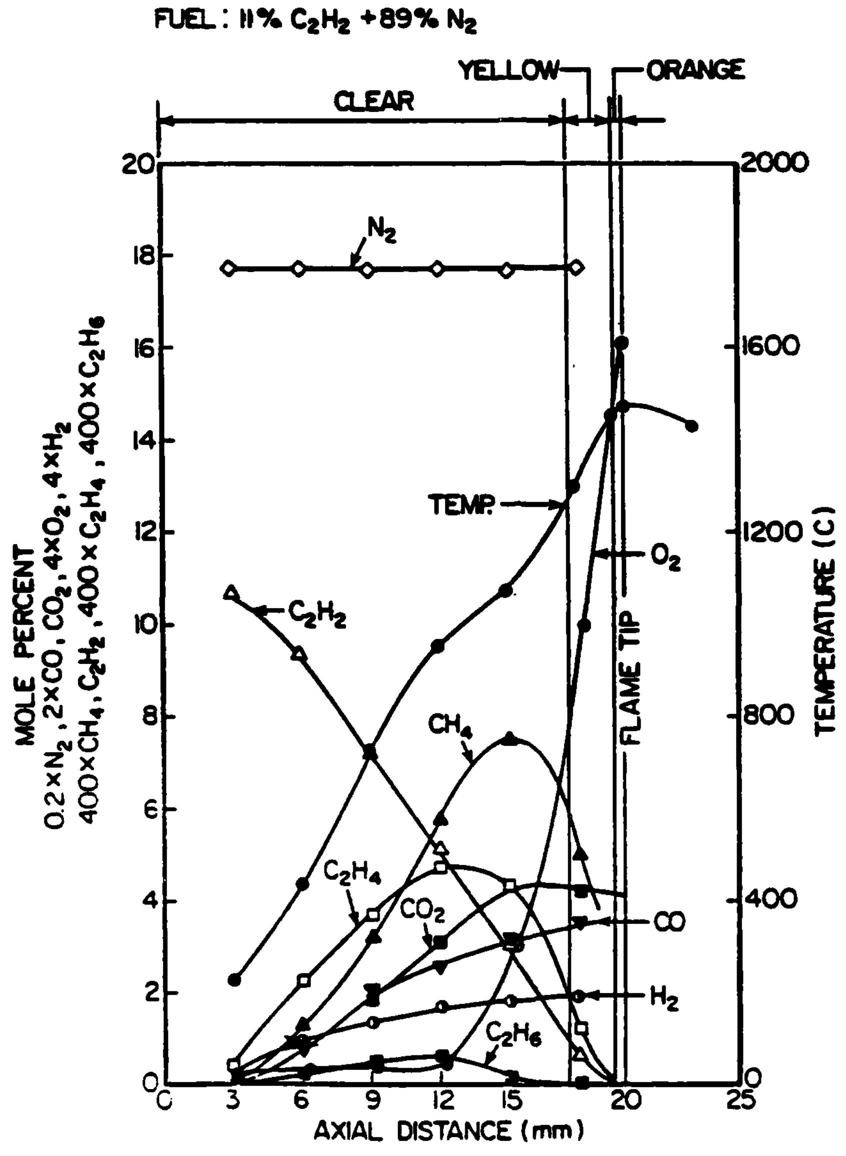

FIGURE 6

Axial profiles of concentration of major species in a laminar diffusion flame burning purified, diluted acetylene (10.8 mole percent) in air. The temperature profile is also shown.

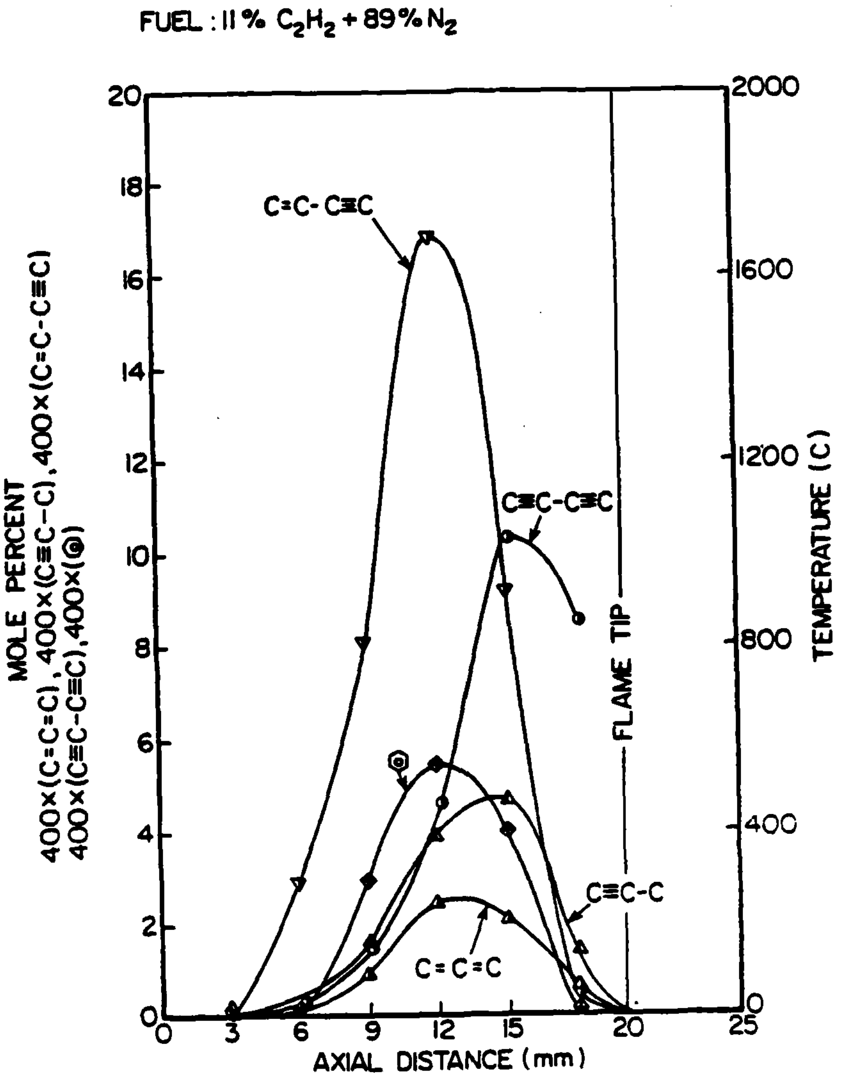

FIGURE 7

Axial profiles of concentration of trace species in a laminar diffusion flame burning purified, diluted acetylene (10.8 mole percent) in air.

CHAPTER IX

ACETONE IMPURITY IN ACETYLENE FROM TANKS

During the experimental studies on the structure of a laminar, co-flowing acetylene diffusion flame as described in Chapter VIII, it was observed that the manufacturer's claim that the purity of research grade acetylene is 99.6 percent is misleading. While the acetylene placed in the tanks is of claimed purity, Commercial manufacturers apparently always dissolve acetylene in acetone in the tank because of safety concerns. Although the acetylene itself in the tank has the claimed purity, the acetylene drawn from the tank is contaminated with acetone, the contamination increasing as the acetylene in the tank is consumed. By use of gas chromatography, between 1 and 20 mole percent of acetone was observed in the gas mixture drawn from the tank. While some investigators are aware of the impurity (Cullis *et al.*, 1967; Tanzawa and Gardiner, 1979) others appear to be unaware of this problem (Bonne *et al.*, 1965; Frenklach *et al.*, 1983, 1985).

The acetone impurity in acetylene was reduced to less than 0.1 mole percent by bubbling the gas mixture through a solution of 125 g of chemically pure sodium iodide in 150 ml of water and then through 250 ml of distilled water. The resulting gas was dried by passing it through a tube containing indicating drierite ($CaSO_4$). As a precaution, the distilled water in the bubbler should be monitored, since the need to change it will be dependent on the acetone concentration. However, the sodium iodide solution was found to be effective even after 20 liters of acetylene has been treated. It was observed that the fresh sodium iodide solution had a faint yellow color initially, which soon disappeared after use. This may be caused by trace iodine impurity, which forms NAI_3; the impurity disappears after acetone has reacted with it.

If the bubblers are ordered such that the distilled water is downstream of the sodium iodide solution, then the purified gas will have a higher moisture content. However, this ensures that any acetone not removed by the sodium iodide solution will be removed by the distilled water. Also, if the sodium iodide bubbler is placed downstream of the distilled water, a reddish glow appears on the outside of the light blue region in the co-flowing diffusion flame. This interesting phenomena must be caused by a gaseous impurity which does not react with $CaSO_4$ but dissolves in water. Even after the NaI solution has been used for some time, the reddish glow appears if the sodium iodide bubbler is placed downstream of the water bubbler. The reddish glow was not observed when the sodium iodide bubbler was placed upstream of the distilled water bubbler.

Dissolved oxygen and oxygen in the space above the surface of the liquid solution in the bubblers were removed by flowing an inert gas at about 0.61/min through the system for ten minutes. The gas in the tank contained about 0.08 mole percent oxygen as an impurity, which may be removed, if necessary, by use of the procedure reported in Cullis *et al.* (1967).

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CHAPTER X

SUMMARY AND CONCLUSIONS

In this chapter the principal findings of this work are summarized and suggestions for future investigation are offered. A theoretical and experimental study of the structure and mechanisms of extinction of laminar diffusion flames is presented. This work is reported in three parts.

In part one, results of studies on the structure and mechanisms of extinction of diffusion flames stabilized in the stagnation point boundary layer that is established when an oxidizing gas stream flows toward the vaporizing surface of a multicomponent liquid fuel is reported. A mixing rule was developed to predict the overall chemical kinetic rate parameters characterizing the gas phase oxidation of diffusion flames burning multicomponent fuels if the overall chemical kinetic rate parameters characterizing combustion of the individual components are known. In order to test the validity of the mixing rule, extinction experiments were performed on diffusion flames stabilized above heptane, toluene, methanol, and a number of homogeneous solutions of these fuels. Experimental and predicted values from the mixing rule for the overall activation energy characterizing the combustion of the fuel blends were found to agree to better than 5 percent. An asymptotic theory is developed which predicts the critical conditions of extinction of a diffusion flame (i.e. the velocity gradient as a function of the oxygen concentration in the oxidizing stream at extinction), burning multicomponent fuels. An explicit algebraic relation was obtained relating the Damköhler Number at extinction to the ambient conditions in the counterflowing streams, thermophysical properties of the reactants and the overall chemical kinetic rate parameters characterizing the gas phase oxidation of pure fuels. In this theory, the chemical reaction is approximated as a one-step process between each component of the fuel and the oxidizer and the activation energy characterizing the reaction is considered to be large in comparison to the thermal energy of the flame. The predictions of the asymptotic theory were compared with results of extinction experiments for blends of heptane and toluene, and were found to be in excellent agreement with experimental measurements. However, for solutions of methanol with toluene and for solutions of heptane, toluene, and methanol the theoretical predictions were slightly different from the experimental measurements. It was suggested that the discrepancy may be due to chemical modification of pyrolysis and oxidation mechanisms of hydrocarbon fuels by methanol.

The influence of alcohols on the combustion of hydrocarbon fuels in diffusion flames was studied. Extinction experiments were performed in diffusion flames burning a variety of alcohol-hydrocarbon fuel blends. Experimental results were interpreted in terms of a previously developed asymptotic theory. The reactivities of various pure fuels and fuel mixtures were compared. Results show that methanol is more reactive than ethanol or butanol. It was observed that the reactivity of a fuel mixture containing heptane and toluene increased with an increasing proportion of methanol.

The detailed structure of diffusion flames burning methanol, heptane, toluene, and blends of these fuels was determined experimentally. The concentration profiles of a number of stable species were measured by use of gas sampling with quartz microprobes. Coated thermocouples were used to measure the profiles of temperature. Results were interpreted by use of the mixture fraction as the independent variable. The position of maximum temperature was measured to be on the fuel side of the diffusion flame in all of the fuels studied. Observation of the fuel concentration at the flame zone suggests that the asymptotic analysis previously developed may be more accurate if modified such that the concentration of fuels are allowed to reach a value of zero at different locations in the flame. A complete asymptotic theory of diffusion flames burning multicomponent fuels would require a more detailed analysis of the structure of laminar flames, including considerations of multiple step chemistry. In addition, the measured composition profiles should be compared with numerical solutions of the conservation equations for energy, momentum, and chemical species in conjunction with detailed chemical kinetic mechanisms.

In part two of this work, the results of theoretical and experimental studies of the structure and mechanisms of extinction of a counterflow partially premixed, diffusion flame is reported. An asymptotic analysis is performed to predict the critical conditions of extinction of this flame. An explicit algebraic expression was obtained relating the Damköhler Number at extinction to the ambient conditions in the counterflowing streams, thermophysical properties of the reactants and the overall chemical kinetic rate parameters characterizing the gas phase oxidation of these fuels. Extinction experiments were performed on a partially premixed, diffusion flame stabilized between a vaporizing surface of heptane and a gaseous stream consisting of methane, oxygen and nitrogen. These experimental measurements were used to deduce the overall chemical kinetic rate parameters characterizing the gas phase oxidation of methane. Comparison of these results with the work of previous investigators shows good agreement. Results of the extinction experiments show that the stability of a heptane diffusion flame is enhanced, as the concentration of methane premixed with the oxidizer stream is increased. Further study of the structure of partially premixed, diffusion flames should allow for a better understanding of the mechanism of flame stabilization, which has possible application in a variety of practical situations.

In part three of this work, results of an experimental study of the structure of coflowing, laminar diffusion flames burning diluted ethane, ethylene, and acetylene in air is determined. A three-stage filtering process was developed to purify acetylene which is normally contaminated with acetone in commercially available gas cylinders. Temperature profiles and composition profiles of a number of stable species were measured in these coflowing diffusion flames. Experimental results are discussed in terms of chemical mechanisms of soot formation. The pyrolysis of ethane and ethylene are observed to lead to acetylene production. The ratio of benzene to acetylene was measured to be lowest in the case of the acetylene flame, which has the highest propensity to soot of all of the fuels tested. Consequently, it is suggested that benzene does not play a direct role in soot production. A consideration of the concentration profiles of hydrogen in these three flames suggest that an interaction occurs between young soot particles and acetylene. Further investigation of the chemical structure of hydrocarbon diffusion flames would improve our understanding of the processes of soot formation.

APPENDIX 1

STUDY OF A PREHEATED FUEL AND A PREHEATED OXIDIZER IN A COUNTERFLOW BURNER

Using the counterflow burner assembly, experiments were performed to determine the effect of preheating the fuel and of preheating the oxidizing gas in order to understand the dynamics of the interaction between the gas phase and the liquid phase during combustion. Preheating of the fuel was achieved by increasing the temperature of the heat exchanger (see Fig. 1 in Chapter II), normally used to cool the bottom of the fuel cup. The fuel used was heptane. The temperature at the surface of the liquid pool and the maximum flame temperature was monitored as the temperature of the water in the heat exchanger was changed. The strain rate and the composition of the oxidizer stream was maintained a constant throughout the experiment. The strain rate was held at a value of 40 $\sec^{-1}$, while the mass fraction of oxygen in the oxidizer stream was held at a constant value of 0.18.

The results are shown in Table 1. The surface temperature of the liquid fuel increases only slightly as the amount of preheating of the fuel increases. The maximum temperature in the flame likewise shows an increase, as heat losses from the flame to the liquid pool (in order to vaporize the liquid fuel) are reduced.

It has been predicted that a counterflow diffusion flame could exhibit instabilitys if the oxidizer stream is preheated (Kerstein, 1984). In order to investigate the effect of preheating of the oxidizer, extinction experiments were performed with methanol as a fuel. The oxidizer was preheated by use of a nichrome wire heater placed in the gas duct. The heating rate of the nichrome wire and thereby the temperature of the oxidizer was controlled by a rheostat. Oxidizer temperature was measured by attaching a thermocouple at the wire mesh screen located at the exit of the duct. Our experiments show that over a wide range of parameters the predicted instabilities of the diffusion flame does not occur.

Extinction results shown in Fig. 1 reveal that for constant strain rates, the oxygen mass fraction at extinction decreases in a near-linear fashion as the screen temperature increases. Table 2 shows that as the oxidizer temperature varies the calculated adiabatic flame temperature immediately before extinction remains essentially the same. This result is consistent with theories which are based on the criterion of a critical Damköhler at extinction. The near linear appearance of the plot in Fig. 1 indicates that for the range of parameters studied, the temperature of the oxidizer stream and the mass fraction of oxygen in the oxidizer stream are compensating effects in terms of the adiabatic flame temperature. These results are consistent with the notion of a Damköhler Number criteria for extinction.

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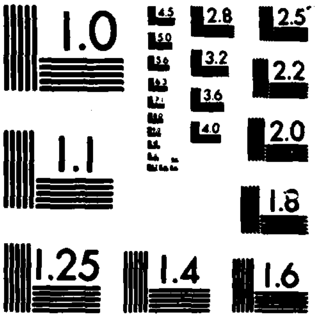

MICROCOPY RESOLUTION TEST CHART
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REFERENCES

A.1. Kerstein, A., Pulsating instability in stagnation combustion. 20th Symposium on Combustion, 1984, 1915-1923.

Temperature of cup bottom (°C)	Temperature of fuel surface (°C)	Temperature of flame °C
18.5	61.5	1223
30.0	63.8	1230
35.1	64.7	1239

TABLE 1

Surface temperature of the liquid fuel surface and the maximum temperature in the flame as a function of the temperature of the bottom of the liquid fuel cup for a flame burning over a condensed pool of heptane under conditions of constant strain rate (40 $\sec^{-1}$) and constant oxygen mass fraction (0.18) in the oxidizer stream.

OXIDIZER TEMP. (K)	ADIABATIC FLAME TEMP. (K)
298	1663
347	1661
368	1661
382	1670
395	1665
420	1675
422	1669
441	1667
465	1669

TABLE 2

Calculated adiabatic flame temperature at extinction Tabulated as a function of the temperature of the oxidizer stream for a diffusion flame burning methanol under conditions of constant strain rates (=46.3 sec^{-1}).

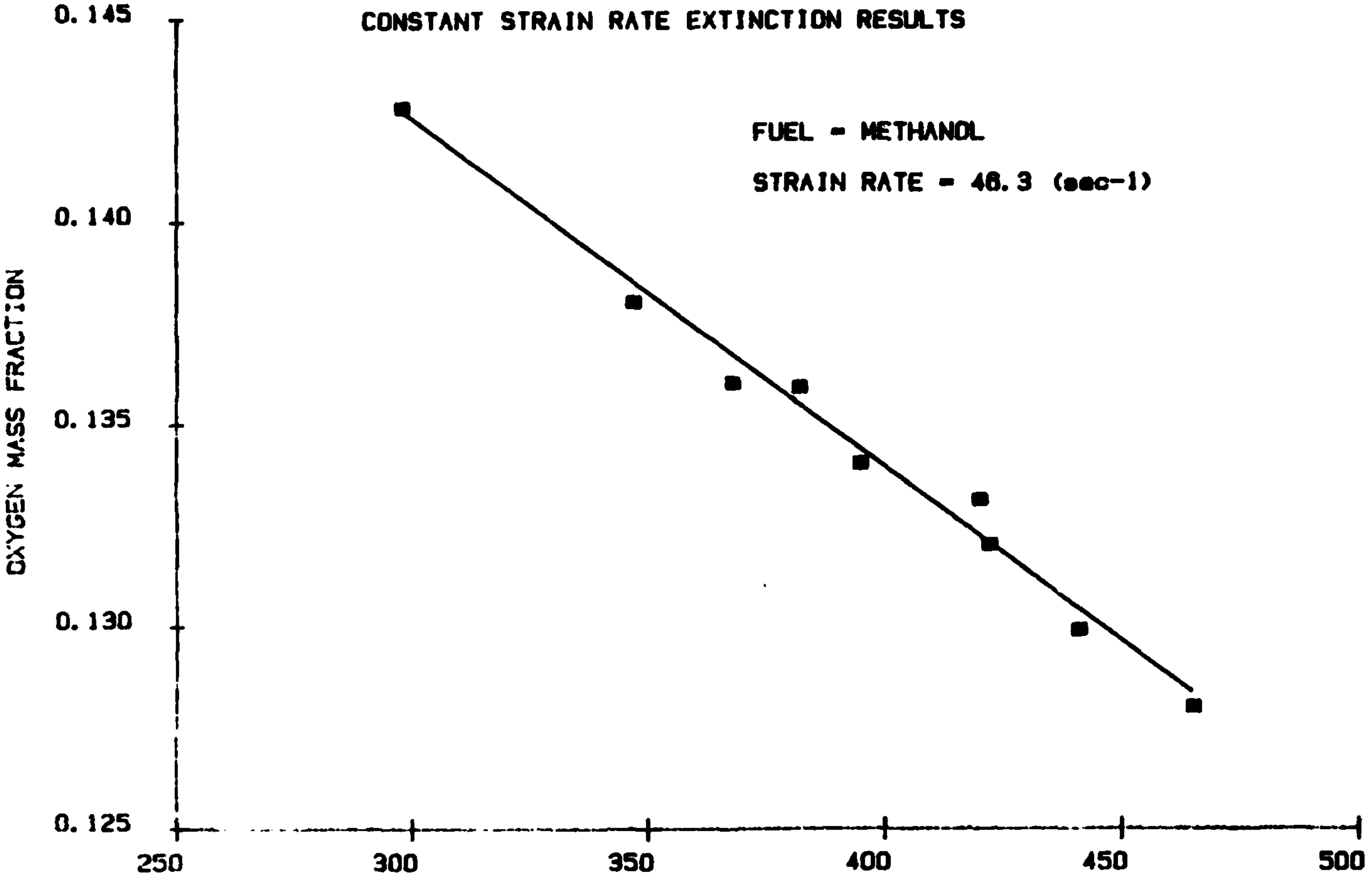

FIGURE 1

Mass fraction of oxygen in the oxidizer stream at extinction as a function of the temperature of the oxidizer stream for a diffusion flame burning methanol under conditions of constant strain rates ($=46.3\ \mathrm{sec}^{-1}$).

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