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The Extinction and Structure of Counterflow Premixed Flames

A thesis submitted in partial satisfaction of the
requirements for the degree Master of Science
in Engineering Sciences
(Chemical Engineering)

by

Jesse Keith Crump

Committee in charge

Professor Kalyanasundaram Seshadri, Chair
Professor Forman Williams
Professor Richard Herz

1989

The thesis of Jesse Keith Crump is approved:

Kalyanasundaram Seshadri

Chair

University of California, San Diego

1989

DEDICATION

This thesis is dedicated to my wife, Lorraine, and two children, Linda and Stacy. Many nights they have spent without their husband/daddy. This work is as much a part of their work and dedication as it is mine.

Table of Contents

List of Symbols

A	Angstroms
a	strain rate (1/sec)
B	frequency factor
cc	cubic centimeter
$C_{or'}$	gradient of progress variable
D	Damkohler number
E	Activation Energy
gc	gas chromatograph
ID	Inside Diameter
M	molecular weight
min	minute
ml	milliliter
psig	pounds per square inch, gauge
R	universal gas constant
SCFM	Standard Cubic Feet per Minute
sec	seconds
T	Temperature
TCD	Thermal Conductivity Detector
V	Velocity (feet/sec)
x	mole fraction
y	mass fraction
α	fuel to oxidizer ratio
Δ	reduced Damkohler number

ρ	density (ml/l)

Subscripts

1	top duct
2	bottom duct
f	fuel
o	oxidizer
s	ambient

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A special thanks goes to the United States Air Force. It is indeed a privilege and honor to serve in the defense of my country. Captain Ujcek, my program manager at the Air Force Institute of Technology, has been of enormous administrative help and assistance. Mention must also go to Air Force ROTC, Detachment 75 at San Diego State. It's always nice to know I wasn't the only Air Force in San Diego.

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What would I have done without Dr. Ishwar Puri. Dr. Puri spent many hours explaining both theory and experimental methods to me. I feel very fortunate for having had the opportunity to work with him.

Lastly, I would like to mention Dr. Venkat Tangirala. Dr. Tangirala provided valuable and objective critique during my experiments.

ABSTRACT OF THE DISSERTATION

The Extinction and Structure of Counterflow Premixed Flames

by

Jesse Keith Crump
Master of Science in Engineering Science
(Chemical Engineering)
University of California, San Diego
Professor Kalyanasundaram Seshadri, Chair

A theoretical and experimental investigation of the extinction of a counterflow premixed flame was performed using methane as the fuel. The extinction limits were measured for a premixed flame stabilized between a premixed, fuel lean stream of methane, air and nitrogen and a stream of hot combustion products. The composition of the reactant mixture as a function of the strain rate was measured at extinction over a wide range of conditions. The results are interpreted using previously developed theories to derive overall chemical kinetic rate parameters. Temperature and composition profiles were obtained for several premixed flames near extinction. The [illegible]. ([illegible])

I Introduction

Theoretical and experimental studies concerning the fundamental heat transport processes, mass transport processes and chemistry in laminar premixed flames are important problems in combustion theory. The phenomena of ignition and extinction of premixed flames have motivated several theoretical and experimental studies over a number of years. In this thesis, I shall report on experimental and theoretical investigation of the mechanisms of extinction of counterflow, laminar, premixed flames.

A number of previous theoretical and experimental studies on the mechanisms of extinction of premixed flames have been concerned with predictions and measurements of concentration and pressure limits of propagation of flammable mixtures in standard tubes (Bregeon et al., 1987; Coward and Jones, 1952; Lovachev, 1979; Mitani and Williams, 1980). Counterflow premixed flames stabilized between opposing streams of a premixed combustible material and an inert gas (or products) have been suggested as a useful tool for theoretical and experimental investigation of extinction limits for laminar flames (Libby and Williams, 1982,1983). In addition, it has been shown that results of studies on counterflow premixed flames are relevant in modelling turbulent combustion (Bray, 1981; Libby and williams, 1982,1983).

The mechanisms of extinction of twin premixed flames have been studied by Sato (1982) and by Law et al. (1986). Twin premixed flames can be stabilized in the laboratory by directing two premixed combustible streams against each other. If the composition of the combustible streams and their velocities at the exit of the ducts are equal, then the stagnation plane would be located equidistant from the ducts and the two premixed flames can be stabilized on either side of the stagnation plane. Critical conditions of extinction of these flames have been measured by Sato (1982) and Law et al. (1986). Depending on the value of the lewis number of the limiting reactant, these flames were either seperated (Lewis number <1) of merged (Lewis number >1) prior to extinction. However, in general, the structure and mechanisms of extinction of twin flames can be different from the structure and mechanisms of extinction of a single premixed flame. Therefore, to address the more fundamental question concerning the structure of premixed flames, experiments were performed on premixed flames stabilized between counterflowing streams of a combustible reactant mixture and an inert stream of high temperature products. The theory developed by Libby and Williams (1982,1983) is used to interpret the results obtained here.

Since the activation energy characterizing the overall combustion process for most fuels encountered in practice is large, matched asymptoic analysis has been employed to analyze the structure of premixed flames (Buckmaster and Mikolaitis, 1982; Libby and Williams, 1982,1983; Libby et al., 1983; Seshadri,1983). Seshadri (1983) analyzed the asymptotic structure of a premixed flame stabilized between two opposing streams. One stream was a premixed combustible and the other stream an inert gas. The chemical reaction was approximated as a one step irreversible process of first order with respect to fuel and oxidizer. Other approximations introduced by Seshadri (1983) were that (a) the flow is inviscid, incompressible and the Mach number is small, (b) the density, specific heat and transport coefficients are constants, (c) diffusion velocities of all species are described by Fick's law and that the diffusivities of mass and heat are equal (implies that the Lewis number is unity), and (d) Defour effects, Soret effects and heat transport by radiation are negligible. The governing conservation equations were found to be similar to those for the counterflow diffusion flame analyzed previously by Linan (1974). The Damkohler number, defined as the ratio of a characteristic diffusion time to a characteristic chemical reaction time was a parameter in this analysis. The characteristic S curve emerges when the maximum flame temperature is plotted as a function of the Damkohler number. Seshadri (1983) obtained criteria for ignition and extinction for these counterflow premixed flames. Libby and Williams (1982, 1983), using activation energy asymptotic, analyzed the characteristics of premixed flames stabilized between counterflowing streams of reactants and products. Assumptions introduced in the analysis were similar to those of Seshadri (1983) except that the density was not assumed to be constant. Isenthalpic flow were the enthalpy of the reactant stream is equal to the enthalpy of the product stream (Libby and Williams, 1982) and nonisenthalpic flow (Libby and Williams, 1983) were considered. For the case .were the enthalpy of the product stream is less than the enthalpy of the reactant stream for low rates of strain, the flame was stabilized on the reactant side of the stagnation plane. As the rate of strain is increased, at the critical rate of strain or Damkohler number, an abrupt transition of flame location from the reactant side to the product side was observed. This transition was interpreted by Libby and Williams (1983) as extinction.

Recent theoretic studies by Peters and Williams (1987) and Seshadri and Peters (1989) have used reduced chemical kinetic mechanisms to analyze the structure of unstretched, laminar premixed flames. The asymptotic structure identified in these analysis depend on the competition between rate coefficient of different elementary reactions, since the activation energy of the elemental reactions entering into the analysis are not large. However, in the absence of similar asymptotic analysis for stretched, laminar, premixed flames, attempts will be made to interpret the experimental results using large activation energy asymptotic analysis which assume the the overall chemical reaction proceeds by a one step reaction.

Experiments have been performed by Zamfirescu et al. (1987) on premixed flames stabilized between counterflow streams of premixed reactant and hot products and the critical conditions of extinction were measured. Here we report measurements over a wide parametric range and also the results of the measurement of the concentration profile of various stable species in the flame and the temperature profiles.

The theoretical model used to interpret the experiments is summarized in Section II. The experimental apparatus is described in Section III. The experimental results and their interpretation is given in Sections IV through VI. The conclusions are summarized in section VII.

II Theory

Libby and Williams (1982,1983) have described the theory of predicting the critical conditions of extinction of counterflow premixed flames. The gas phase chemical reaction is approximated as a one step irreversible process yielding carbon dioxide and water. The activation energy, E, is assumed to be a large quantity in comparison to the thermal energy in the flame. The results identified as "nearly adiabatic flows" by Libby and Williams (1983) were used to interpret the experimental results. At extinction, the analysis of Libby and Williams (1983) show that

$$\Delta = (((-C_{or}')^2 \, T_s^3)/(2 \, T_f^3)) \; \exp(4/(-C_{or}')^2) \qquad (1)$$

where Δ is the reduced Damkohler number and $-C_{or}'$ is the gradient of the progress variable evaluated at the reaction zone. T_s is the ambient temperature and T_f is the adiabatic flame temperature. Libby and Williams (1982) have plotted $-C_{or}'$ as a function of τ and η_r where τ equals (Tf/Ts)-1 and η_r is the similarity variable. For extinction, Libby and Williams have found that η_r is 0 (the flame moves across the stagnation plane at extinction). Libby and Williams (1983) have also shown that

$$\Delta = D\,\varepsilon^2 \exp(-\,T_a/T_f) \qquad (2)$$

where ε is a small quantity equal to $(T_f\ T_s/T_a\ (T_f\text{-}T_s))$ and T_a is the activation temperature equal to -E/R where E is the activation energy and

R is the universal gas constant. The term D is the Damkohler number, equal to $B_{of}\ \rho_s\ T_s/(2\ T_f\ M_f\ a)$ where B_{of} is the frequency factor of the reaction rate, M_f is the molecular weight of the fuel and a is the strain rate at extinction.

Equations 1 and 2 can be combined to yield

$$\ln((\rho_s\ F\ T_s{}^3)/(2\ T_f{}^3\ D\ \varepsilon^2)) = -T_a/T_f \qquad (3)$$

where ρ_s is the ambient gas density and F is defined by

$$F=((-Cor')^2/\rho_s)\ \exp(4/(-C_{or}')^2) \qquad (4)$$

Substitution of the Damkohler number in equation 3 yields

$$\ln((a\ F\ (T_f\text{-}T_s)^2/T_f{}^4) + \ln(M_f\ T_a{}^2/B_{of}) = -T_a/T_f \quad (5)$$

This equation is an "arrhenius type" equation and was used to determine the activation energy and frequency factor.

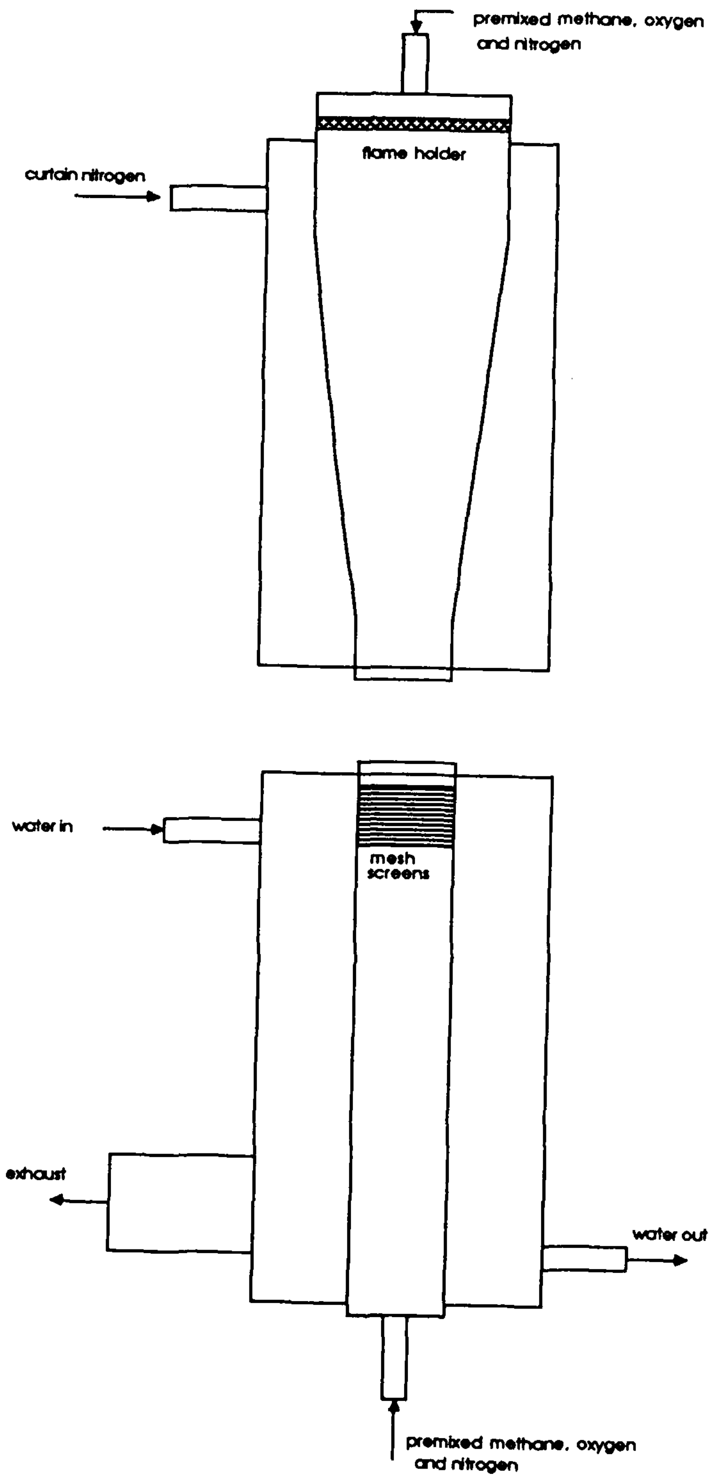
III Apparatus

A schematic of the burner used in these experiments is shown in figure 1. The burner consists of two 2.54 cm I.D. ducts. These ducts are separated by a distance of 1.4859 cm using three spacer rings on the collar of the burner. These spacer rings also serve to keep the centerlines of the ducts aligned. Gaseous flow is then introduced through these ducts. The bottom duct has several mesh screens (20 - 150 mesh/inch) to insure a laminar flat velocity profile. The top duct was tapered to minimize turbulence and obtain a flat velocity profile.

A diffusion flame was lit upon introducing air from the top duct and methane from the bottom duct. A premixed flame was then ignited inside the top duct by introducing methane into the top duct of the burner, creating a partially premixed flame. The partially premixed flame would travel up into the top duct and result in a premixed flame with hot inert products of combustion exiting from the top duct. Air was next added from the bottom duct and a premixed flame was established between the two ducts of the burner. A suction was applied around the bottom duct to pull the products of combustion. These products were then cooled in a heat exchanger which surrounded the

Figure 1.

Schematic of burner.


premixed methane, oxygen and nitrogen
curtain nitrogen
flame holder
water in
mesh screens
exhaust
water out
premixed methane, oxygen and nitrogen

bottom duct. To isolate the flame from the surrounding atmosphere and prevent further combustion in the heat exchanger, a curtain of nitrogen was applied from around the top duct.

The gas handling system was designed to allow any flow rate and composition from either the top or bottom ducts. Fischer and Porter variable area flowmeters were used to measure the flow rate of each component. By using different density floats and diameter flowmeters, the desired flow rates of each component were able to be measured. Low to moderate flow rate flowmeters were calibrated using a wet test meter. A Princeton calibrated flowmeter was used to calibrate flowmeters used for high volumetric flow rates (air flow through bottom duct). Pressure gauges were used in parallel with the flowmeters to maintain 10 psig pressure at the entrance of each flowmeter. Therefore, the flowmeters were not affected by fluctuations from the gas cylinders or pressure changes when adjusting other component's flow rates.

IV Extinction Experiments / Results

The temperature of the hot inert products of combustion exiting from the top duct was fixed at 971 and 1006 ^{o}C. The ratio of fuel to oxygen (α) was fixed at 0.35 for the top duct stream. The velocity at the top duct was kept fixed. α was then fixed for the unreacted gasous stream exiting from the bottom duct. Nitrogen was slowly added to the bottom duct stream until an abrupt extinction occured. The bottom premixed flame was then relite and the experiment repeated twice to verify the results.

A series of extinction experiments were performed using different bottom duct fuel/oxygen velocities while keeping the top duct velocity and α for both ducts constant. As the velocity of the bottom stream increased, the flame moved up toward the top duct. Extinction data was collected over a range of bottom duct velocities. To confirm that there were no heat losses to either of the two ducts, temperature profiles were measured at the extremums and the slope of these temperature profiles were negligibly small near the ducts.

The velocity of the top stream was next increased while keeping α and the top temperature constant. The top duct temperature was much more sensitive to the exit velocity changes than to changes in the composition (diluting nitrogen). This was due to radial heat losses inside the top duct. The radial temperature gradient resulting from these heat losses became negligible within 3 mm from the tip of the top duct. The increase in top duct exit velocity pushed the premixed flame sheet down toward the bottom duct and additional extinction experiments were performed. To verify that the changes in top duct exit velocity and composition did not change the extinction results, several data points were overlapped for the two top duct exit velocities.

As α for the bottom duct approached 0.5 (stoichiometry), the extinction results became erratic and the experimental scatter increased. Therefore, the results for α equal to 0.475 and 0.5 were not used. To confirm that this scatter was not a result of excess oxygen from the top duct diffusing through the stagnation plane, the experiments were repeated using α equal to 0.5 for both ducts. No decrease in experimental scatter resulted and so the results were not used.

Seshadri and Williams (1978) have shown that the strain rate (a) at extinction can be calculated from the expression

$$a=((-V_2)/L)(1+(V_1/(-V_2)(\rho_1/\rho_2)^{0.5})$$

where L is the distance between the two ducts, V is the gas stream velocity and ρ is the gas stream density.

Figures 2 and 3 show the strain rate verses fuel mole fraction with α maintained constant along each curve. The region below the curve represents extinction and above the curve represents combustion. All curves are least square fits. The curve for the top temperature of $1006^{o}C$ and α equal to 0.452 does not include the last data point shown. The uncertainty of the strain rate calculation was estimated to be 5% and the uncertainty in the mole fraction is 5%.

The strain rate at extinction was not significantly different, at constant oxygen mole fraction, for the two top duct temperatures. Therefore, the "nearly adiabatic" theory developed by Libby and Williams is assumed valid. Using the extinction data and the theory developed by Libby and Williams (1983), Arrhenius type plots were generated. These plots are shown in figures 4 and 5. Table 1 shows the activation energy, E, and the frequency factor, B_{of}, for each of the top duct gas temperatures and fuel to oxygen ratio, α, at the bottom duct.

The extinction experiments were next repeated for a variety of top duct temperatures. α for the top and bottom duct streams were maintained constant at 0.35 and 0.400 respectively. The

Figure 2.

Velocity gradient as a function of fuel mole fraction at the tip of the bottom duct at extinction with α held constant and the temperature at the tip of the top duct at 971°C.

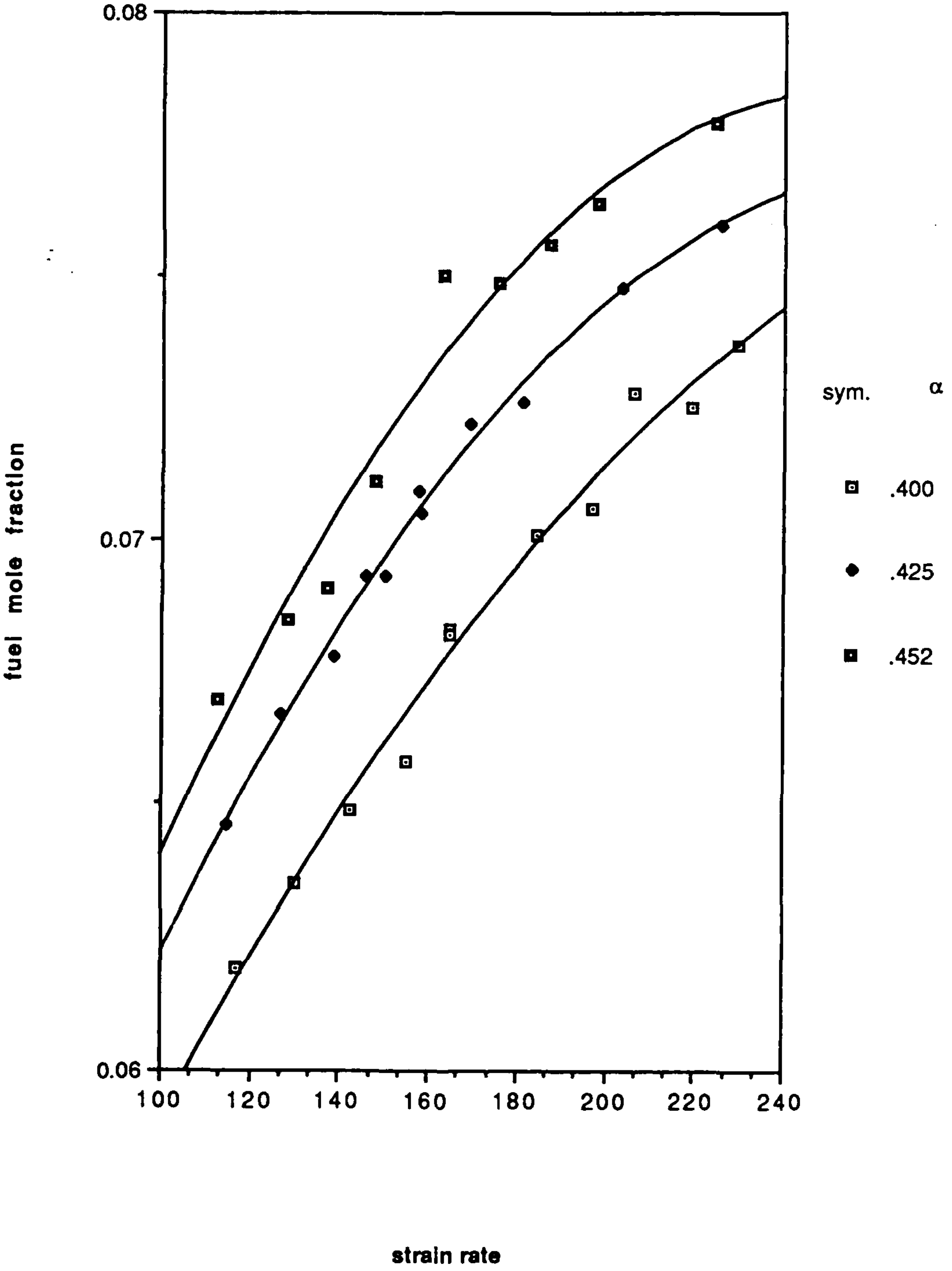

0.08
0.07
0.06
100
120
140
160
180
200
220
240
fuel mole fraction
strain rate
sym.
α
.400
.425
.452

Figure 3.

Velocity gradient as a function of fuel mole fraction at the tip of the bottom duct at extinction with α held constant and the temperature at the tip of the top duct at 1006°C

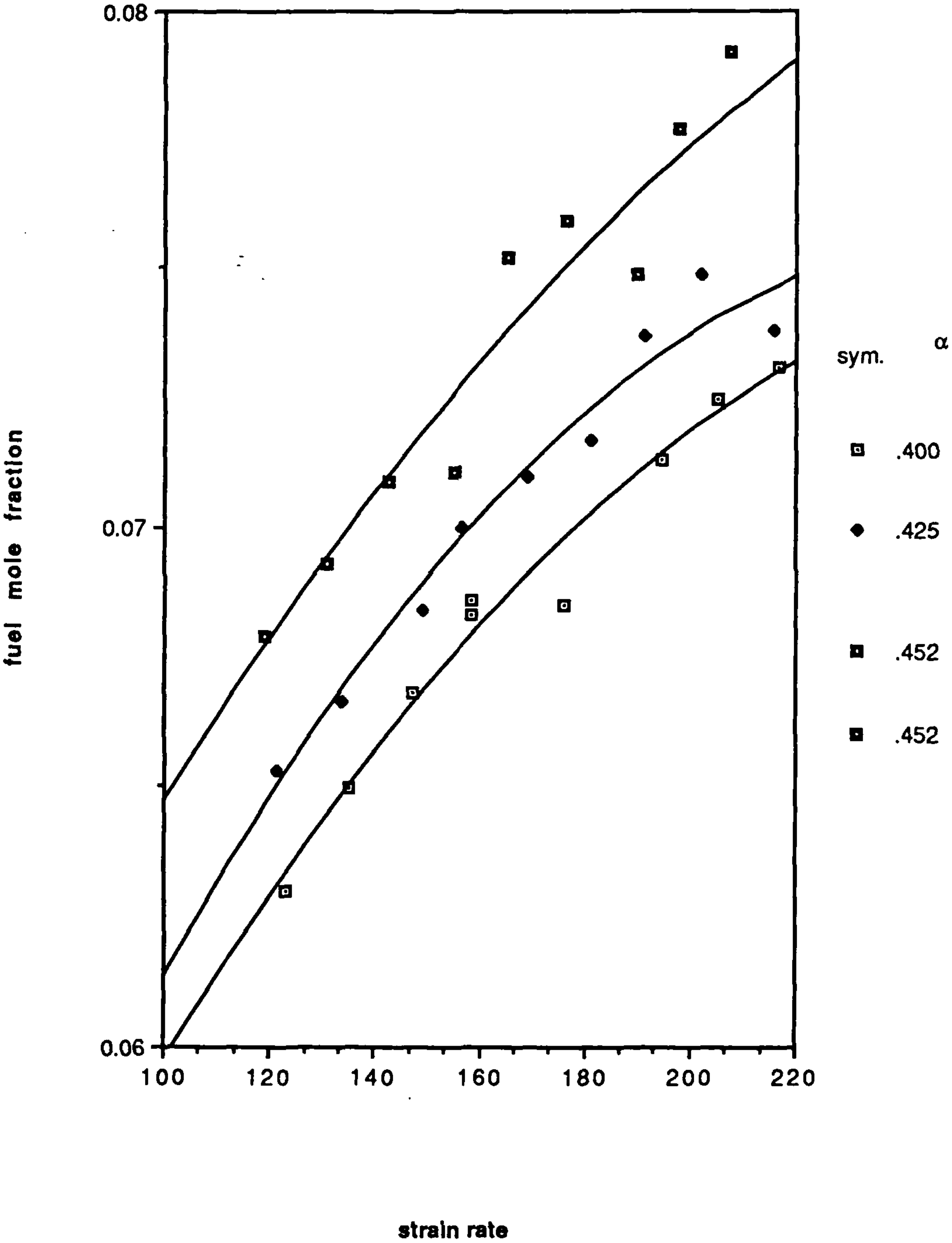

0.08
0.07
0.06
100
120
140
160
180
200
220
fuel mole fraction
strain rate
sym.
α
.400
.425
.452
.452

Figure 4.

Arrhenius type plot for the temperature at the top duct at 971°C and α equal to .400, .425 and .452.

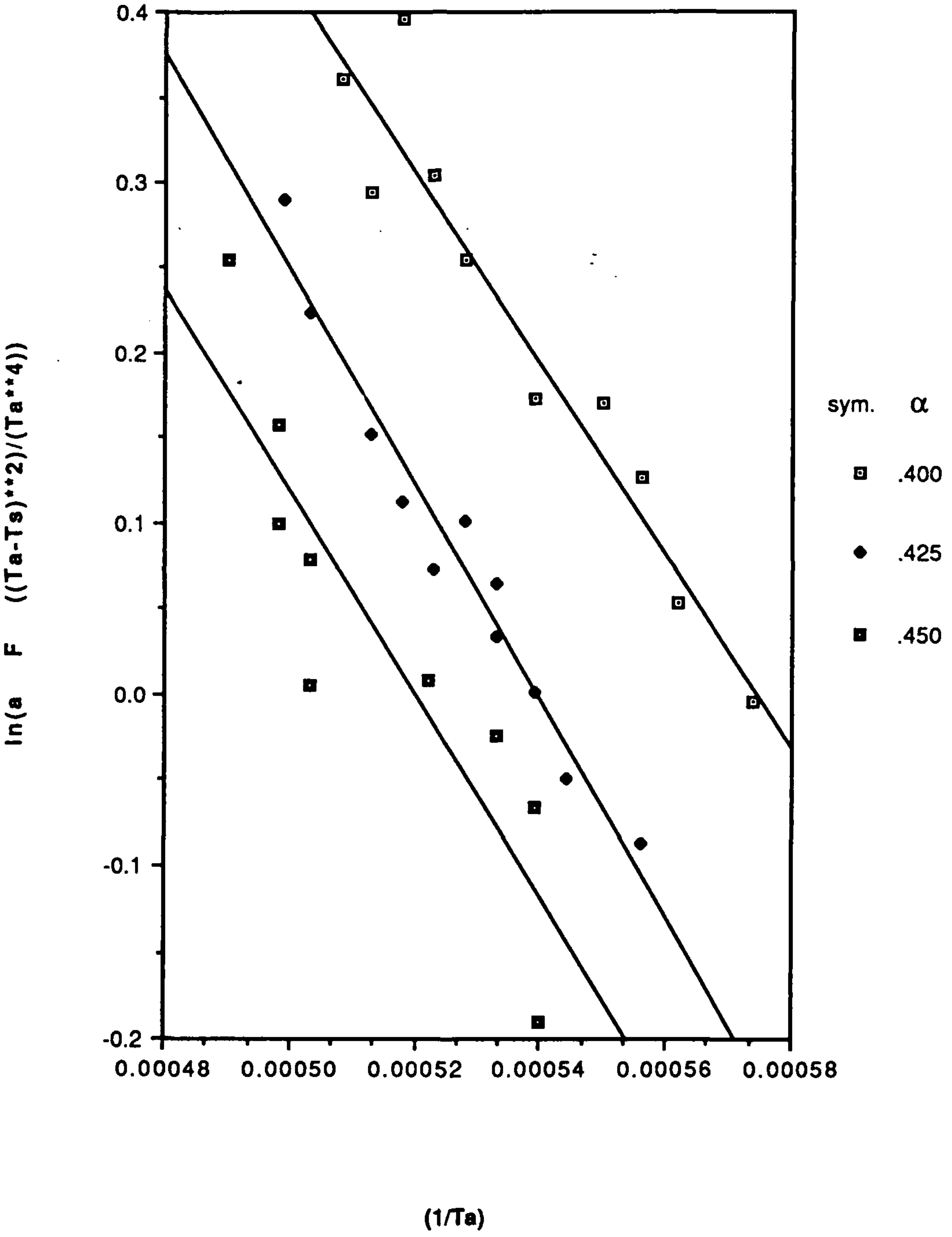

0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
ln(a F ((Ta-Ts)**2)/(Ta**4))
0.00048
0.00050
0.00052
0.00054
0.00056
0.00058
(1/Ta)
sym. α
▫ .400
◆ .425
■ .450

Figure 5.

Arrhenius type plot for the temperature at the top duct at 1006^{o}C and α equal to .400, .425 and .452.

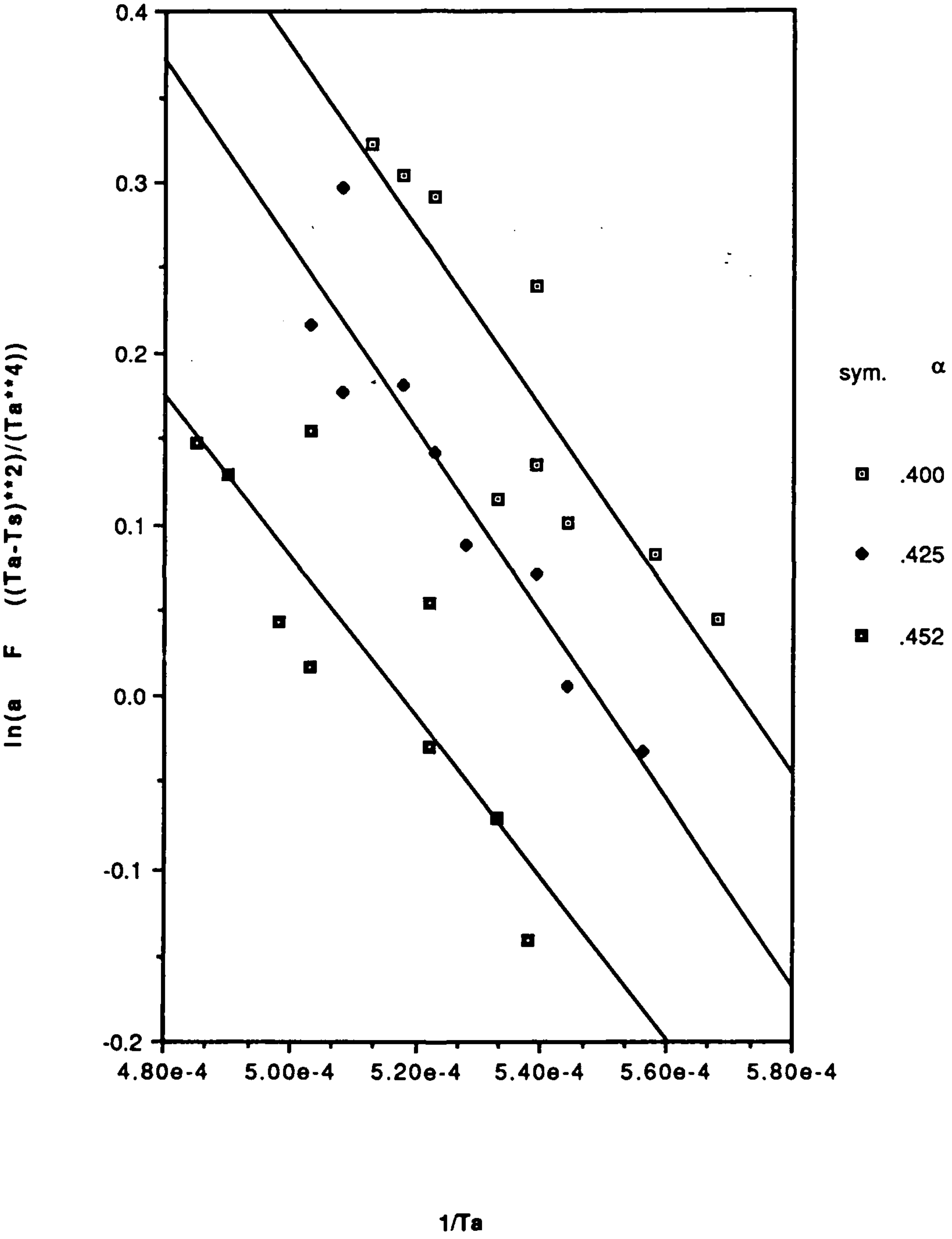

0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
4.80e-4
5.00e-4
5.20e-4
5.40e-4
5.60e-4
5.80e-4
ln(a F ((Ta-Ts)**2)/(Ta**4))
1/Ta
sym. α
□ .400
◆ .425
■ .452

Table 1.

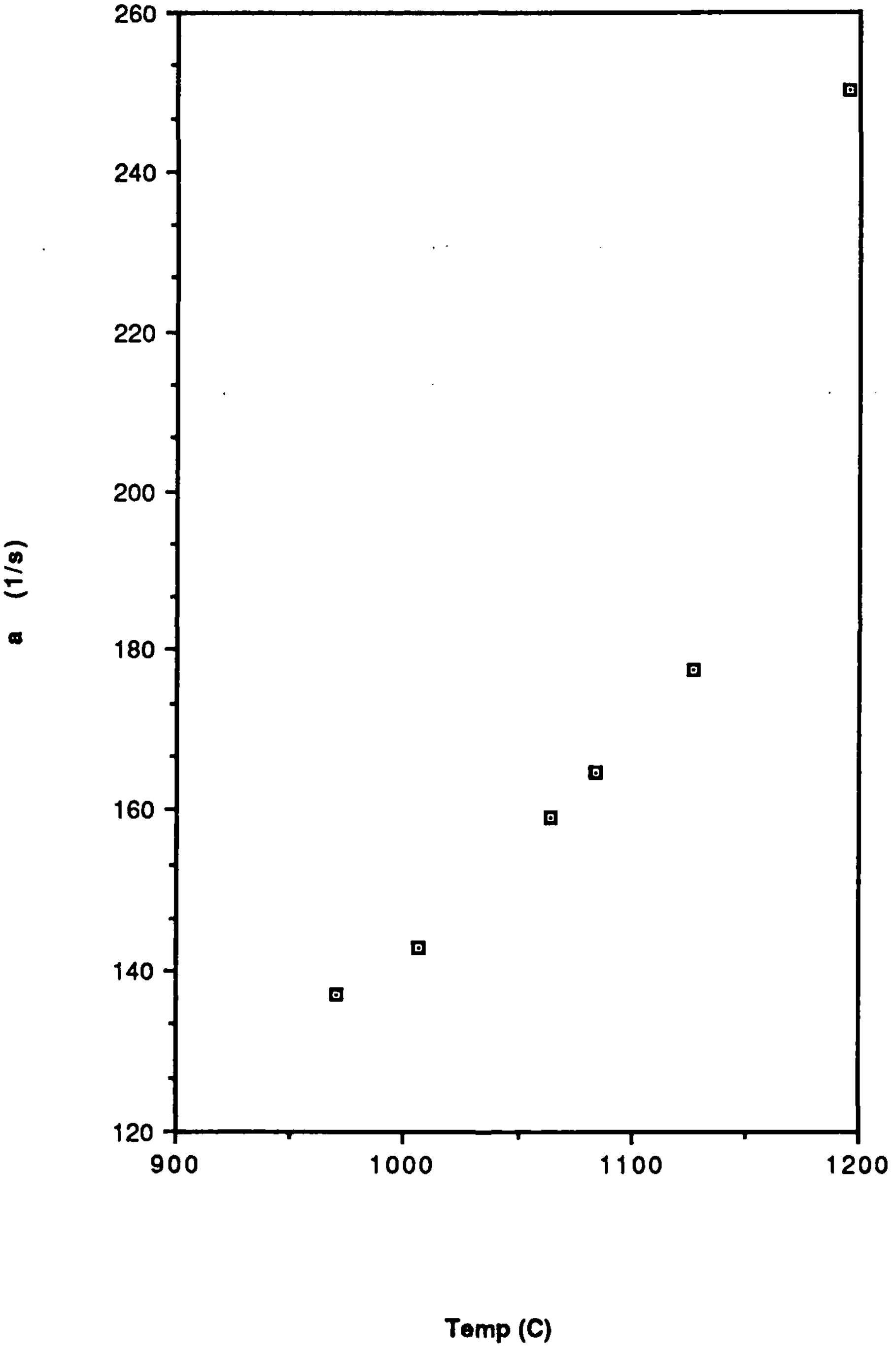
Activation Energy, E, and frequency factor, B_{of}, for the top duct temperature of 971°C and 1006°C and α equal to .400, .425 and .452.

	971 C	1006 C
α = .400	E = 11.1 kcal/mole	E = 10.5 kcal/mole
	B_{of}=1.26*10^{10} cm^3/mole/s	B_{of}=9.35*$10^{9}$$cm^3$/mole/s
α = .425	E = 12.6 kcal/mole	E = 10.7 Kcal/mole
	B_{of}=1.94*10^{10} cm^3/mole/s	B_{of}=8.99*10^{9} cm^3/mole/s
α = .452	E = 11.8 kcal/mole	E = 9.3 kcal/mole
	B_{of}=1.25*10^{10} cm^3/mole/s	B_{of}=3.93*10^{9} cm^3/mole/s

top duct velocity and temperature was kept fixed while the bottom stream velocity was slowly increased until an abrupt extinction occured. The bottom stream oxygen mole fraction was kept constant at 0.164 during the experiments. All data were reproduced three times to verify the results. It was found that for a top stream gas temperature of 1195^{o}C or above, no abrupt extinction occured. The results of these experiments are found in figure 6.

Figure 6.

Strain rate, a, as a function of top duct temperature with the bottom duct oxygen mole fraction equal to 0.164 and α for the top and bottom duct equal to .35 and .400 respectively.


260
240
220
200
180
160
140
120
a (1/s)
900
1000
1100
1200
Temp (C)

V Temperature Profiles

To determine if the measured values of the critical conditions of flame extinction are influenced by heat losses to the screens in the ducts, temperature profiles were obtained using .003 inch diameter Platinum verses Platinum-10% Rhodium thermocouples (type S). An Omega electronic ice point (model MCJ) was used as a thermocouple reference junction. Data was recorded using an Omniscribe strip chart recorder. The thermocouple was positioned using an X-Y micromanipulator and a cathotometer, which has a reading accuracy of

To prevent catalytic effects, the thermocouple wire was coated with Yttrium Oxide (Kent 1970). The Yttrium Oxide was made into a paste and "painted" onto the thermocouple wire. The coating was then slowly heated to leave a thin coat of Yttrium Oxide. After heating, the thermocouple was examined under a microscope to check for uniform coating and the absence of thermal cracking from the heating process.

A very thin thermocouple wire was required to prevent the thermocouple from acting as a flame holder. The thermocouple was slowly raised from the bottom duct while observing for distortions in the flame due to the thermocouple. The data was then retaken by lowering the thermocouple from the top duct, once again observing for flame distortion. The two profiles were then pasted together for the final temperature profile. The distortion was found to occur only over a distance of 0.3 mm in the flame and could be eliminated by the above method. All thermocouple data was corrected for radiative heat losses by the method used by Seshadri and Rosner (1984). Two thermocouples, one coated with Yttrium Oxide and one uncoated, were placed in the same position above a flame. Since the Yttrium Oxide has a different emittance than the bare platinum (.28 vs .20), different temperatures were recorded. The radial temperature profile in the flame was measured and found to be negligible . Since the conduction losses were small (thermocouples lie within an isotherm), convection equals radiative losses.

$$(ck/(d)^{0.5})(T_g-T_t) = \varepsilon\ \sigma\ (Tt^4 - 298^4)$$

where d is the thermocouple diameter, T_g is the gas temperature and T_t is the thermocouple temperature. σ is the stefan-boltzmann constant, ε is the emissivity, and $ck/(d)^{0.5}$ is related to the nusselt number. Since T_{t1} does not equal T_{t2} but T_g is the same for both thermocouples, the above equation can be rearranged to equal

$$T_g=(T_{t1} - c\ T_{t2})/(1-c) \qquad (6)$$

where the subscript t1 and t2 denote the coated and uncoated thermocouples and c is equal to

$$c=(d_1/d_2)^{0.5}(\varepsilon_1/\varepsilon_2)(T_{t1}{}^4-298^4)/T_{t2}{}^4-298^4) \qquad (7)$$

Once the gas temperature is known, equation 6 can be rearranged to yield

$$T_g=T_{t1} + \text{const}\ (T_{t1}{}^4-298^4) \qquad (8)$$

Seshadri and Rosner (1984) have shown that the const in equation 8 is constant over a wide range of temperatures.

The slopes of the temperature profiles near the exit of the ducts are nearly zero. Hence, the heat losses to the screens in the duct are negligibly small. In the vicinity of the luminous zone, the gradients of temperature are steep, especially on the preheat zone side of the flame. Therefore, the measured temperature profiles show that the reaction zone is thin.

The temperature verse distance from the bottom duct for α equals .400 and .452 and the top duct gas temperatures of 971 and 1006°C are shown in figures 7 and 8.

Figure 7.

Temperature profiles for a temperature at the top duct of $971^{o}C$ and α equal to .400 and .452.

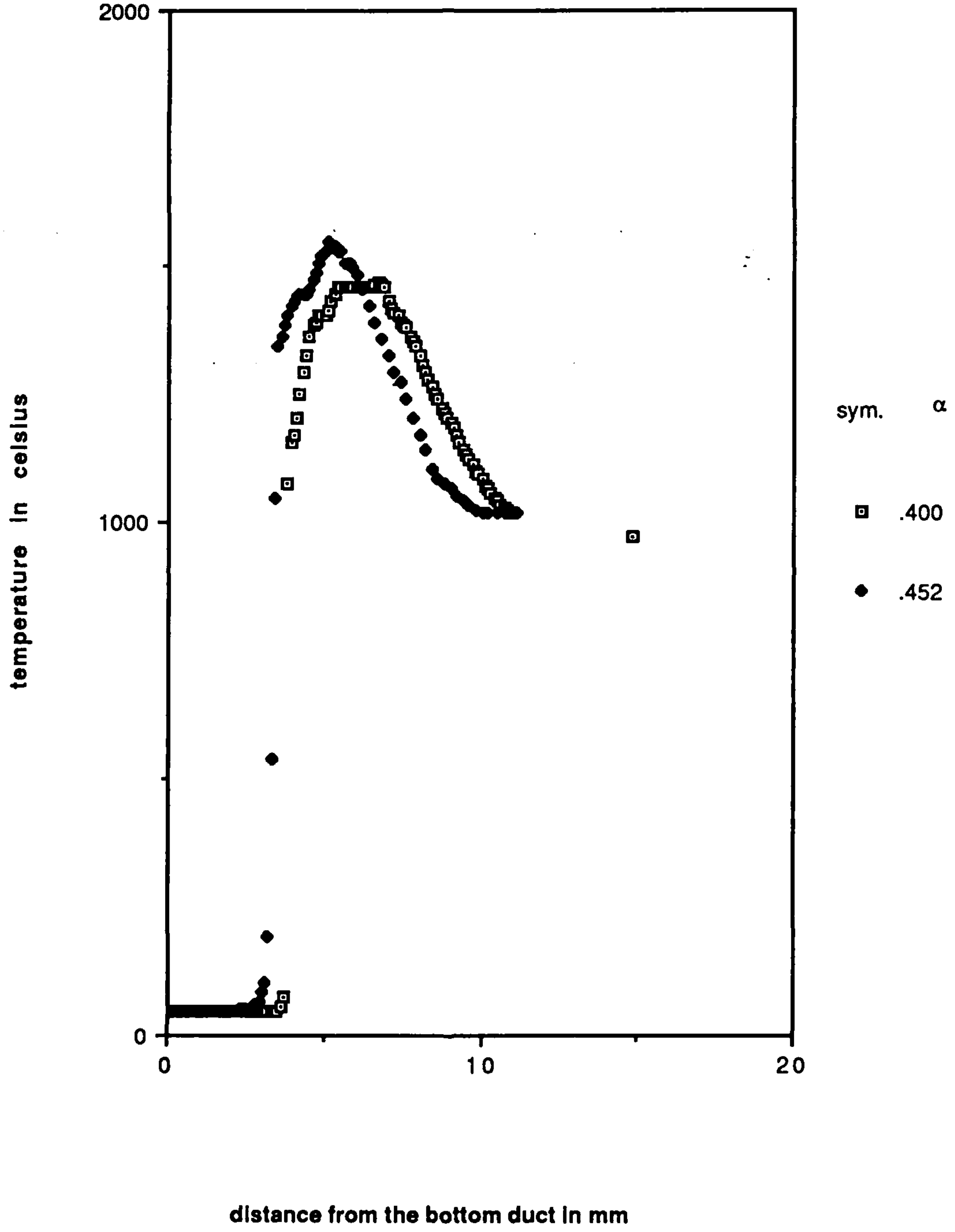
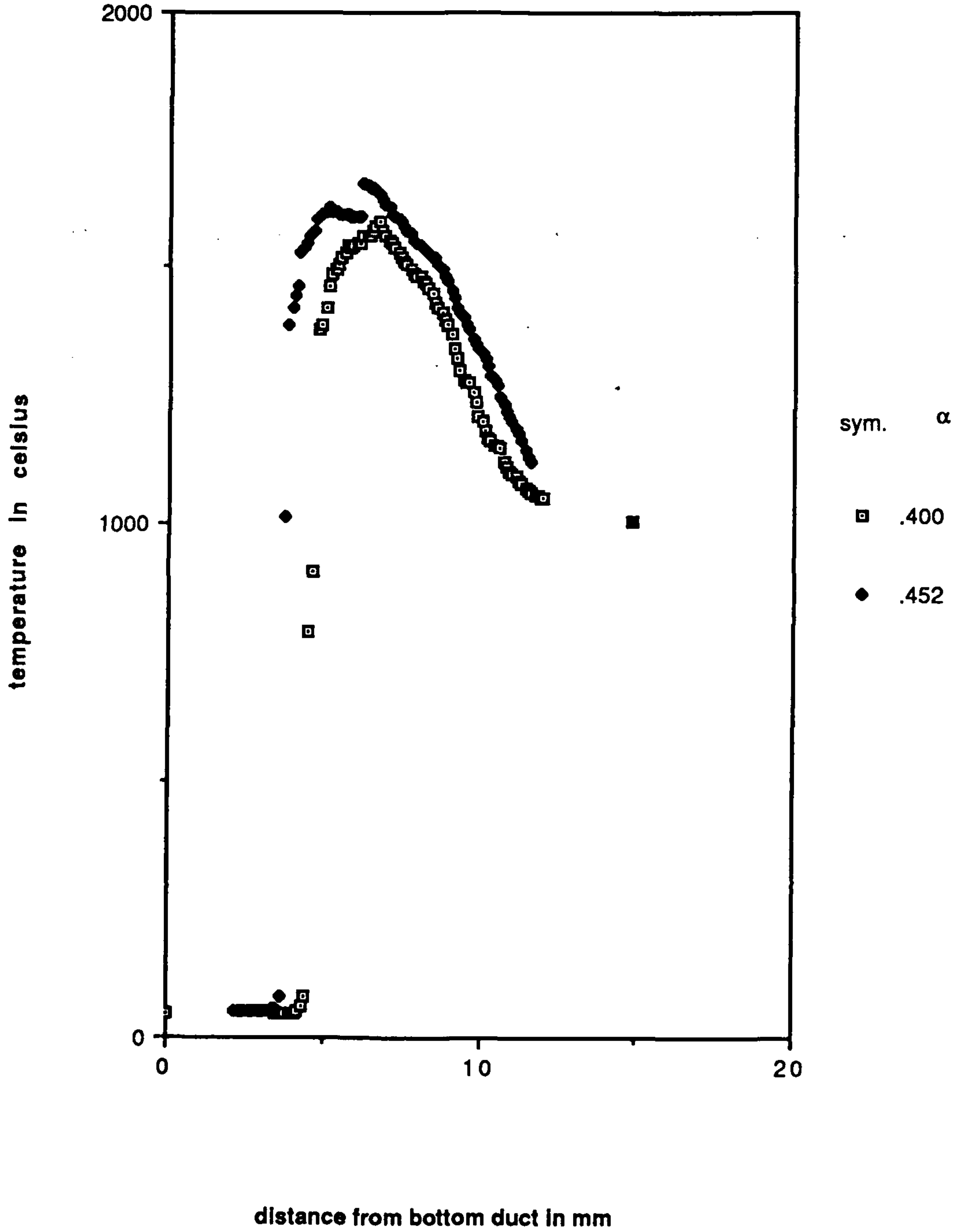

2000
1000
0
0
10
20
temperature in celsius
distance from the bottom duct in mm
sym.
α
□ .400
◆ .452

Figure 8.

Temperature profiles for a temperature at the top duct of 1006^{o}C and α equal to .400 and .452.


2000
1000
0
0
10
20
temperature in celsius
distance from bottom duct in mm
sym.
α
▣ .400
◆ .452

VI Gas Chromatograph Experiments/ Results

Composition profiles were measured using a gas chromatograph. Gas samples were taken from the flame using a quartz probe with a nozzle diameter of 125 A. The quartz probe was positioned using a x-y micromanipulator and cathotometer. A down stream pressure of 100 torr was established with a vacuum pump. This pressure insured chocked flow with sonic velocities at the probe tip followed by supersonic flow immediately behind the tip of the probe. The supersonic flow is needed to provide rapid cooling of the combustion products as well as to prevent pressure effects in the flame due to gas sampling. Heat tape was used on the gas collection plumbing to prevent condensation of the less volatile components.

The quartz probe was bent at a right angle and lowered vertically into the flame for all distances 8.9 mm and closer to the bottom duct. This was necessary to prevent the probe from acting as a flame holder and distorting/extinguishinging the flame. At distances above 8.9 mm, the probe was inserted vertically into the burner.

The sample collection loop was flushed with helium . The gas sample was then collected for 5 minutes to completely fill the collection loop. After the sample of combustion products was taken, the sample loop was then pressurized to atmospheric pressure using helium gas. The gas chromatograph has a sample loop of 1 cc volume.

Helium was used for both the carrier gas and TCD reference flow. Flow rates for both the carrier and TCD reference stream was adjusted to 30 ml/min. The gas chromatograph column temperature was maintained at 65 degrees centigrade. Sample separation was achieved by using molecular sieve (5 A) and porapak Q columns. The sample was introduced at 0.5 minutes into the gas chromatograph run. At 1.8 minutes, the porapak was taken out of series to trap the heavier hydrocarbons and prevent their entry into the molecular sieve column. The molecular sieve then eluted hydrogen, oxygen, nitrogen, methane and carbon monoxide gases. At 14 minutes, the molecular sieve was taken out of series and the porapak was placed back into series. The porapak then separated carbon dioxide, ethylene, ethane, water, propylene and propane gases. Table 2 shows sample elution times.

Sample detection was made using a thermal conductivity detector (TCD). The TCD was calibrated using a known nine gas sample for the hydrocarbons and hydrogen, and atmospheric air for oxygen. Water vaper was calibrated at the top duct exit.

Table 2.

Sample elution times for the gas chromatograph with a flow rate of 30 ml/min and a column temperature of 65°C using molecular sieve and Porapak Q columns.

Sample	Elution Time	Calibration Factor
Hydrogen	2.2	0.41
Oxygen	3.0	0.97
Nitrogen	4.3	1.00
Methane	5.9	0.08
Carbon Monoxide	11.0	0.10
Carbon Dioxide	15.4	0.07
Ethylene	16.1	0.07
Ethane	16.7	0.05
Water	18.9	0.32

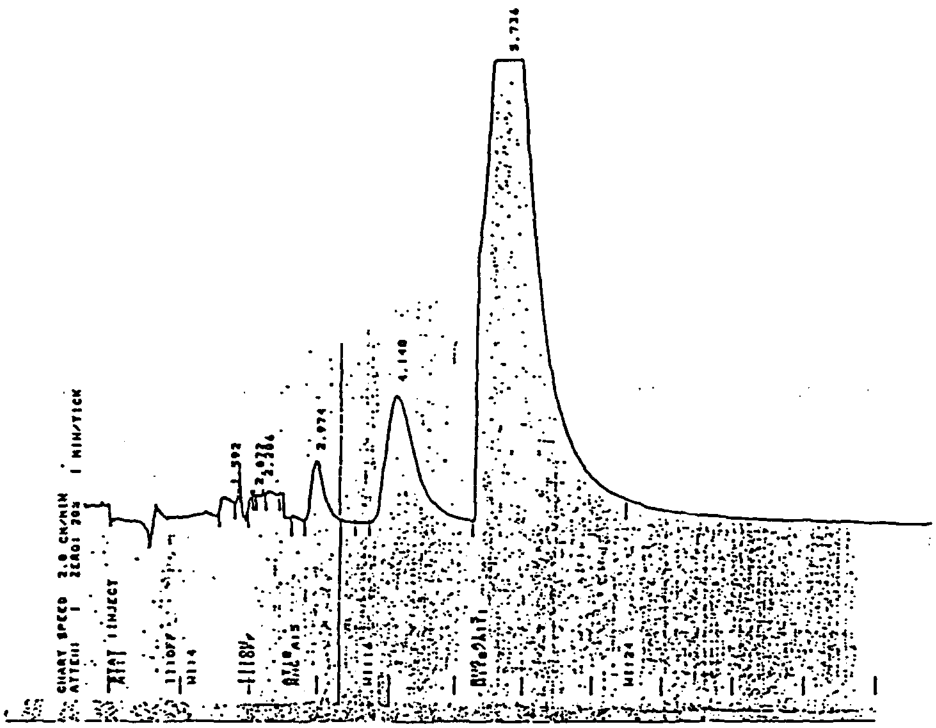
From stoichiometry, water vaper should be present at twice the mole fraction of carbon dioxide. The temperature at the top duct was sufficiently low to ensure no unstable species were present. The position of the top duct was at a distance great enough from the stagnation plane that diffusion from the bottom duct was negligible. All calibrations were done using nitrogen as a reference (calibration factor of 1.)

Figure 9 shows a chromatogram taken for α equal to 0.4, the top duct temperature at 971°C and at a distance of 5.0 mm from the bottom duct. Figures 10 and 11 show the composition profiles of various species in the flame near extinction verses the distance from the bottom duct for α equals .400 and a temperature of 971°C.

Comparing figures 7 and 10 show that the concentration of methane and oxygen decrease rapidly at the location where the temperature and the concentrations of carbon dioxide and water rise rapidly. This behavior is consistent with the classical structure of premixed flames. The profile of oxygen decreases rapidly at the reaction zone and slowly increases toward the top duct. However, the concentration of oxygen is nonzero everywhere, indicating that the limiting reactant is methane. The mole fraction of water is nearly twice that of carbon dioxide, which is consistent with the stoichiometry of the overall reaction of methane and oxygen.

Figure 9

Sample gas chromatograph output.



```
TITLE: SAMPLEGAS CALIBRATION                   20:13     5 DEC 83

CHANNEL NO: 1      SAMPLE: 5.0 BOTTOM       METHOD: VENKAT

PEAK  PEAK            RESULT      TIME        AREA    SEP
 NO   NAME            MOLE %      (MIN)       COUNTS  CODE
   1                  0.0000      1.592         224   BB
   2                  0.0000      2.023          62   BV
   3                  0.0000      2.072          59   VV
   4  H2              0.0483      2.206          77   VB
   5                  0.0000      2.618         221   BV
   6  O2             16.9996      2.974       11600   VB
   7  N2             76.7525      4.148       50916   BV
   8  CH4             6.0651      5.736       49373   VB
   9  CO2             0.1449     15.109        1308   BB

TOTALS:             100.0000                 113862

MULTIPLIER: 1.00000

SAVED FILE: N2+H20084

ERRORS:
  DSK LIMIT

RUN LOG:                     TIME:
  COL   :65                   0.00
  LIMIT:170                   0.00
  INJ A:110                   0.00
  INJ B:110                   0.00
  ION   :44                   0.00
  TCD   :160                  0.00
  AUX   :10                   0.00
  FLOWA:                      0.00
  FLOWB:                      0.00
  DET A:TCD                   0.00
  DET B:NONE                  0.00
  RNG A:.05                   0.00
  RNG B:NONE                  0.00
  VOL A:1                     0.00
  VOL B:1                     0.00
  A/STA:0.01                  0.00
  A/STB:0.01                  0.00
 —GC XE:NONE         -------.0.00  --
  TCFIL:164                   0.00
  STAT :INJECT                0.00
  RNG A:5                     2.60
 —RNG A:.5                    5.30
  RNG A:.3                   12.20
  RNG A:.5                   13.00
  STAT :RESET                26.85

NOTES:
  PCRB OUT AT 1.8 MIN
  MOLS OUT AT 14.0 MIN
  PCRB IN AT 15.0
  65° C.  INJECT AT 0.5 MIN
```

Figure 10.

Composition profiles of nitrogen, oxygen, carbon dioxide, water and methane for α equal to .400 and a temperature of 971^{o}C at the tip of the top duct.

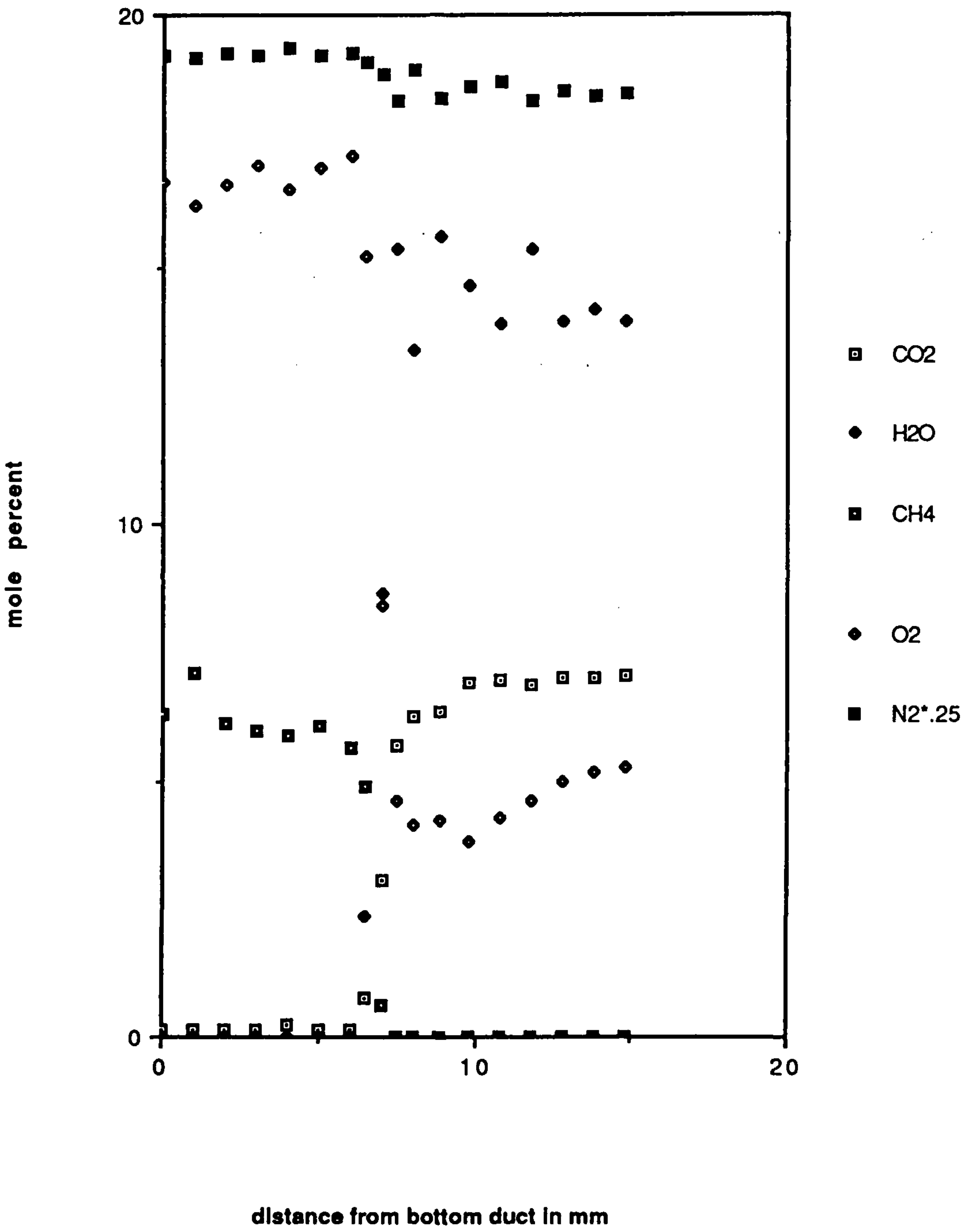
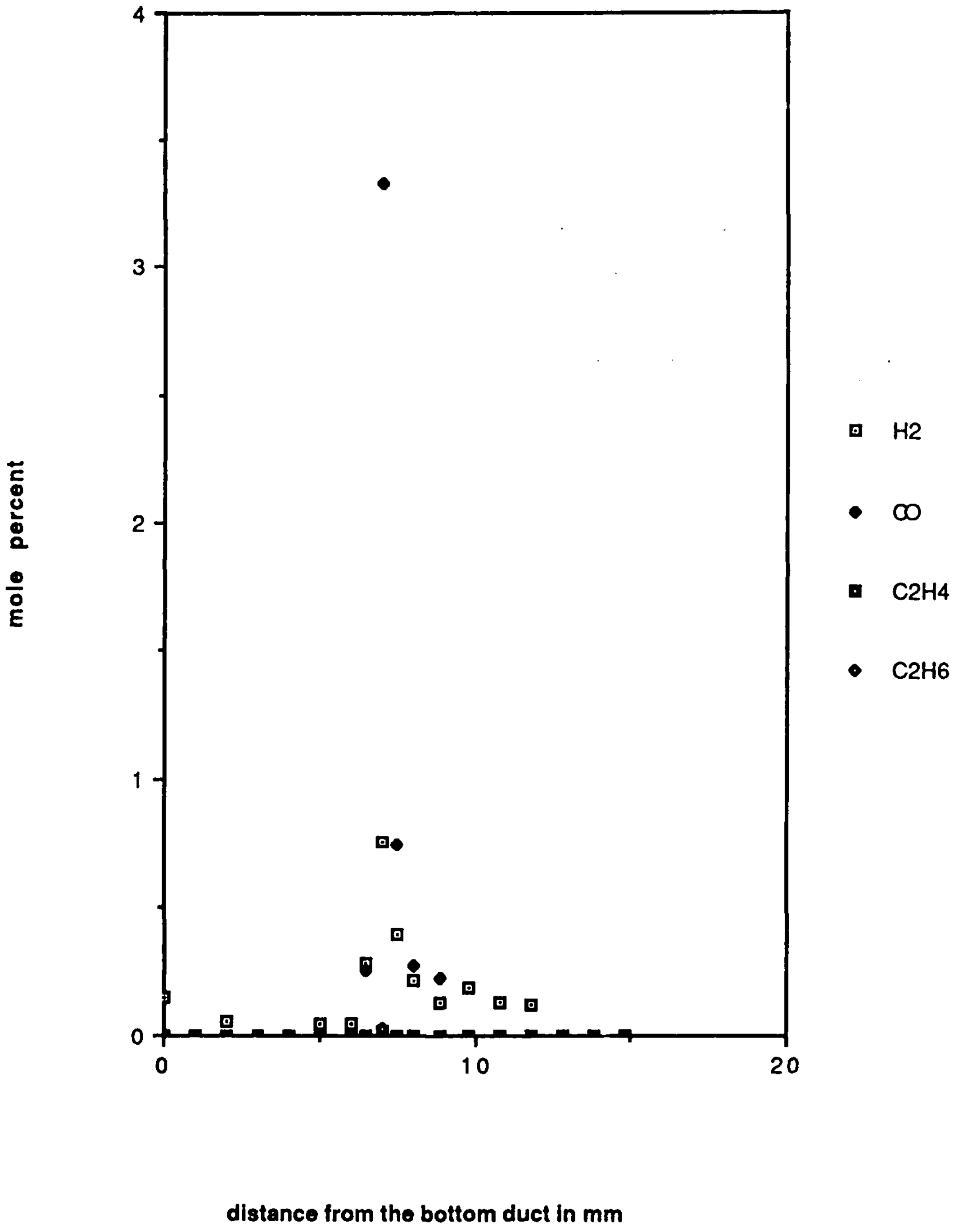

mole percent
20
10
0
0
10
20
distance from bottom duct in mm
CO2
H2O
CH4
O2
N2*.25

Figure 11.

Composition profiles of hydrogen, carbon monoxide, ethane and ethylene for a temperature of 971^{o}C at the tip of the top duct and α equal to .400.


mole percent
4
3
2
1
0
0
10
20
distance from the bottom duct in mm
H2
CO
C2H4
C2H6

VII Conclusions

The overall chemical kinetic rate parameters obtained using the results of the extinction experiments, listed in table 1, show that the activaton energy decreases with increasing values of the temperature of the hot products stream. The overall chemical kinetic rate parameters obtained from the results of the extinction experiments on methane - air diffusion flames have been reported to be E equal to 40 Kcal/mole (Seshadri and Trevino 1989); for premixed flames, deduced from the results of extinction experiments on partially premixed flames, the activation energy was found to be 40 Kcal/mole (Hamins, et al, 1985). For premixed flames deduced from experimental results where the product stream was replaced by nitrogen issuing from a duct at an ambient temperature of 298 K, to be E equal to 43 Kcal/mole (Puri and Seshadri 1987). Also in the present set of experiments, abrupt extinction was not observed if the product stream temperature was increased above 1195°C, which implies that E is equal to 0. Hence there appears to be a tendency for the activation energy to decrease with increasing values of the temperature of the product stream. Asymptotic theories where the chemistry is approximated by a one step overall process will fail to predict this behavior. Hence, this phenomena is due to multistep chemistry in the flame.

An important finding of this work is that, if the hot product stream temperature is increased above 1195°C, an abrupt extinction does not occur. B. Rogg (1988) had performed numerical calculations to determine the structure of counterflow premixed flames stabilized between counterflowing streams of a reactive mixture of methane and air and hot equilibrium products. Rogg (1988) did not obtain a converged solution for values of the strain rate above 2280 s^{-1}. We are unable to confirm this prediction because such large rates of strain cannot be obtained in the laboratory. Recently, Peters and Williams (1987) and Seshadri and Peters (1989) had analyzed the structure of an unstretched methane - air flame using a reduced chemical kinetic mechanism to describe the gas phase oxidation of methane. The asymptotic analysis shows that the inner structure of these flames consist of a thin fuel consumption layer where the fuel is attacked by the radicals to form carbon monoxide and hydrogen. Outside the fuel consumption layer exists a broader hydrogen/carbon monoxide oxidation layer where these compounds are oxidized to form water and carbon dioxide. Some of these features assumed by these analysis are supported by the experimental results. Comparing figures 10 and 11 show that the maximum values of hydrogen and carbon monoxide occur at the point where the concentration of methane is nearly zero, and therefore this must be the location of the fuel consumption layer. To accurately analyze the experimental results obtained here, an asymptotic analysis of stretched premixed flames using multistep chemistry must be developed.

References

Bray, K.N.C. (1981) Turbulent Flows with Premixed Reactants, Turbulent Reacting Flows, P.A. Libby and F.A. Williams (Eds.). Springer-Verlag, p. 115.

Bregeon, B., Gordon, A.S.,and Williams, F.A. (1978). Near Limit Downward Propagation of Hydrogen and Methane Flames in Oxygen-Nitrogen Mixtures. Combust. Flame, 33, 33.

Buckmaster, J.D., and Mikolaitis, D. (1982). The Premixed Flame in a Counterflow. Cumbust. Flame 47, 191.

Coward, H.F., and Jones, G.W. (1952). Limits of Flammability of Gases and Vapors, Bulletin 503, Bureau of Mines, Washington D.C.

Hamins, A. (1985). The Structure and Extinction of Diffusion Flames. Ph.D. Thesis, University of California, San Diego.

Hamins, A., Thridandam, H., and Seshadri, K. (1985). Structure and Extinction of a Counterflow Partially Premixed, Diffusion Flame. Chem. Engrg. Sci. 40, 2027.

Kent, J.A. (1970). A Non-catalytic Coating for Platinum-Rhodium Thermocouples. Combust. Flame, 14, 279.

Law, C.K., Zhu, D.L., and Yu, G. (1986). Propagation and Extinction of Stretched Premixed Flames. Twenty-Second Symposium (International) on Combustion. The Combustion Institute.

Libby, P.A., Linan, A., and Williams, F.A. (1983). Strained Premixed Laminar Flames with Nonunity Lewis Numbers. Combust. Sci. Tech.
34, 257.

Libby, P.A., and Williams, F.A. (1982). Structure of Laminar Flamelets in Premixed Turbulent Flames. Combust. Flame 44, 287.

Libby, P.A., and Williams, F.A. (1983). Strained Premixed Laminar Flames under Nonadiabatic Conditions. Combust. Sci. Tech. 31,1.

Linan, A. (1974). The Asymptotic Structure of Counterflow Diffusion Flames for Large Activation Energies. Acta Astronautica 1,1007.

Lovachev, L.A. (1979). Flammability Limits - A Review. Combust. Sci. Tech. 20, 209.

Mitani, T., and Williams, F.A. (1980). Studies of Cellular Flames in Hydrogen - Oxygen - Nitrogen Mixtures. Combust. Flame 39, 169.

Peters, N., and Williams, F.A. (1987). The Asymptotic Structure of Stoichiometric Methane - Air Flames. Combust. Flame 68, 185.

Puri, I. (1987). The Structure and Extinction of Counterflow Flames. Ph.D. Thesis, University of California, San Diego.

Puri, I.K., and Seshadri, K. (1986). Extinction of Diffusion Flames Burning Dilute Methane and Dilute propane in Diluted Air. Combust. Flame 65,137.

Rogg, B. (1988). Response and Flamelet Structure of Stretched Premixed Methane - Air Flames. 73, 45.

Puri, I.K., and Seshadri, K. (1987). The Extinction of Counterflow Premixed Flames Burning Diluted Methane-Air , and Diluted Propane-Air Mixtures. Combust. Sci. and Tech. 53, 55.

Sato, J. (1982). Effects of Lewis Number on Extinction Behavior of Premixed Flames in a Stagnation Flow. Nineteenth Symposium (International) on Combustion. The Combustion Institute, p. 1541.

Seshadri, K. (1977). Studies of Flame Extinction. Ph.D. Thesis, University of California, San Diego.

Seshadri, K. (1983). The Asympotic Structure of a Counterflow Premixed Flame for Large Activation Energies. Int. J. Engng. Sci. 21,103.

Seshadri, K. and Peters, N. (1989). The Inner Structure of Methane - Air Flames. Submitted for Publication in Combust. Flame.

Seshadri, K., and Rosner, D.E. (1984). Optical Methods and Results of Dew Point and Deposition Rate Measurements in Salt/Ash Containing Combustion Gas. B2O3(l) Disposition Rates by Interference Method and Comparison with Theory. AIChE. J. 30,187.

Seshadri, K., and Trevino, C. (1989). The Influence of the Lewis Numbers of the Reactants on the Asymptotic Structure of Counterflow Diffusion Flames. submitted to Combust. Sci. and Tech.

Seshadri, K., and Williams, F.A. (1978). Laminar Flow between Parallel Plates with Injection of a Reactant at High Reynolds Number. Int. J. Heat Mass Trans. 21,251

Zamfirescu, N., Puri, I.K., and Seshadri, K. (1987). The Extinction of Counterflow Premixed Flames Burning Diluted Methane - Air Mixtures. Paper 2B-027, Joint Conference, Western States and Japanese Sections of the Combustion Institute, 1987 Fall Meeting, Honolulu, Hawaii. p.88