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To be presented at the 18th International
Symposium on Combustion, Waterloo, Canada,
August 18-22, 1980

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FLOW DIFFUSION FLAME

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August, 1980

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FLOW DIFFUSION FLAME

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ABSTRACT

An opposed flow diffusion flame was used to study the burning characteristics and flame structure of high purity poly(ethylene) near extinction conditions. Special attention was paid in the experimental design to insure a uniform oxidizer velocity profile which is essential for burning conditions near extinction. The influence of the sampling probe on the location of the flame was studied through the use of shear interferometry.

Structural measurements were obtained and compared with other investigations of diffusion flames. Departures from the commonly assumed collapsed flame model of laminar diffusion flames were observed in terms of excessive CO concentrations and oxygen penetration into the fuel side of the flame. An upper bound on the importance of oxygen diffusion to the fuel surface and subsequent surface oxidation was placed at twenty percent of the energy required for fuel pyrolysis, with the remainder of the energy being delivered to the surface from the flame through heat transfer processes.

As the oxygen concentration in the oxidizer flow was decreased and extinction conditions approached, the CO/CO₂ ratio at the flame increased slightly, the oxygen concentration at the luminous flame zone decreased, the flame stand-off distance decreased, and the flame temperature decreased.

Radial similarity in the composition and temperature profiles was established experimentally which confirms predictions and greatly simplifies the modeling of the opposed flow diffusion flame.

INTRODUCTION

Increased utilization of polymeric materials has resulted from their versatility, low cost and availability. This enhanced usage has focused attention upon the fire hazard arising from their inherent flammability. It is anticipated that a better understanding of the mechanism of polymer combustion, particularly in the diffusion controlled regime characteristic of actual fires, will improve the ability to reduce polymer flammability. The current study was undertaken to acquire an improved understanding of the mechanism of polymer combustion through a determination of the flame structure of poly(ethylene) opposed flow diffusion flames. In particular, flame structure was determined at various stages in the approach to extinction to provide information concerning the role of chemistry, and at different radial positions to verify the similarity of reacting flow in the radial direction.

It is also of interest to compare our own findings with those of others to determine whether or not systematic trends emerge from structural studies. There has been considerable research effort devoted to the determination of flame structure of premixed flames; however, relatively little effort has been expended for comparable measurements in diffusion flames. There have been even fewer determinations of flame structure for fuels burning in the opposed flow diffusion flame (OFDF) configuration. Pandya and Weinberg¹ determined temperature and heat release rate profiles of ethylene/nitrogen/oxygen OFDF. Tsuji and Yamaoka² investigated changes in composition of propane and methane OFDF for various oxidizer velocities and oxygen concentrations. The flame

structure of solid fuels burning in the OFDF has been reported by Richard et al.,³ and Seshadri and Williams.⁴

Theoretical descriptions^{5,6,7} of the OFDF have also been given. Each of these invokes the flame sheet approximation of Burke and Schumann⁸ to simplify the description and render model calculations tractable. Flame structure is easily predicted for these models since the flame is assumed to occur along a surface which is the locus of the stoichiometric composition with an infinitesimally thin reaction zone. It is worthwhile to investigate experimentally whether or not deviations from predicted model behavior are found for poly(ethylene) burning in an OFDF.

The experimental and analytical systems used for the measurement of flame structure are described in the second portion of the paper. Flame structure was determined for three molar ratios of oxygen to nitrogen. The oxidizer velocity was 0.48 m/s. Results are compared to other experimental measurements and theoretical predictions whenever possible and these are discussed in the remaining sections of the paper.

THE EXPERIMENTAL SYSTEM

The steady-state combustion of poly(ethylene) was investigated in the opposed flow diffusion burner which is shown schematically in Fig. 1. The burner has been described in detail previously.^{7,9,10} Briefly, an oxidizing mixture of nitrogen and oxygen flowed through an aerodynamic nozzle and impinged on the surface of a solid fuel sample which in steady-state combustion produces a fuel stream opposing the oxidizer flow. An automatic feed control was used to advance the burning fuel sample thereby maintaining the stagnation plane and flame zone at fixed locations.

It is important that the nozzle flow be uniform for combustion studies at or near extinction since non-uniformities lead to localized blow-out and ill-defined extinction velocity. In addition, the possibility of modeling the combustion characteristics of this experiment are greatly enhanced if the flow from the nozzle is laminar. A nozzle was designed and fabricated according to the wind tunnel design of Morel¹¹ to achieve the desirable characteristics. To assess nozzle performance, velocity and turbulent intensity profiles were measured with a hot wire anemometer for a range of velocities at the nozzle exit. Figure 2 shows typical profiles of velocity and turbulent intensity as a function of radial position for an exit velocity of 2.6 m/s. The velocity profile is flat to within a three percent maximum deviation over the region encompassing the sample and the standard deviation of velocity over the sample region is 1.5 percent. A slightly skewed velocity profile results since a single spray tube used to introduce gas into the nozzle

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Figure 1. Opposed flow diffusion flame apparatus for the study of polymer combustion.

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Figure 2. Velocity and turbulent intensity profiles for the oxidizer nozzle.

fails to distribute the flow uniformly. The average turbulent intensity of the nozzle flow is 0.55 percent, indicating laminar flow.

Poly(ethylene) was molded in the laboratory to obtain pure samples which burned reproducibly. Low density poly(ethylene) in pellet form, obtained from Aldrich Chemical, was placed in a stainless steel picture frame mold, heated in an oven at 450 K for 2.7 hours, and immediately pressed with a hydraulic press to 3.2 MPa absolute. The molded polymer was then cut into bars which were turned on a lathe to produce cylindrical samples 12.7 mm in diameter.

Samples were extracted from the flame with quartz microprobes designed to provide an aerodynamic quench. If the probe is large relative to the flame stand-off distance, it is difficult to determine composition profiles accurately. Typical poly(ethylene) flame location was 2.0 mm above the fuel surface. The orifice diameter of the microprobe was 75 μm . To determine whether representative sampling was obtained, deflection mapping was utilized to observe the nature and the range of probe disturbance to the flame. Two shear interferograms are presented in Fig. 3 a,b, showing the flame zone without and with the probe, respectively. The flame is located by the maximum deflection and is marked in both cases by a line. The presence of the probe with sample extraction causes the distance of the flame from the surface to decrease approximately ten percent in comparison with the no probe case. The burning rate, to within experimental error, was unaffected by the probe. Further details of the shear interferometry study of probe disturbance effects are reported in Reference 10.

a. Flame without Probe

b. Flame with Probe with Sample Extraction

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Figure 3. Shear interferograms comparing the flame zone without and with the sample probe.

The probe position was controlled by a Brinkman MS-II-E three axis micrometer which was accurate to 0.01 mm. The probe to surface reference distance was determined optically to within ± 0.10 mm. This uncertainty is one of the major sources of error in the profile measurements. The probe-surface distance of interest is the distance between the melt on the polymer surface and probe. Char nodules form on the melt and they, rather than the melt, are sensed by the helium laser/photodiode system. An improper designation of the polymer surface can result in a distance measurement that is erroneously low.

After extraction from the flame, the sample flowed through a heated line to a Hewlett Packard 5751B gas chromatograph modified to include a column switching system. Samples were injected with a Poropak Q column and Molecular Sieve 5A column in series. The light gases, H_2 , N_2 , O_2 , CO and CH_4 were convected into the MS 5A column and stored while the CO_2 , H_2O and hydrocarbons were eluted from the Poropak Q column into the TC and FID detectors. The output from the TC and FID detectors was simultaneously integrated with an Autolab System IV integrator. The GC was calibrated before and after each run with calibration gases mixed in the laboratory using the partial pressure technique. Concentrations of the calibration gases were verified with mass spectrometry. Multiple samples of the various calibration gases were injected into the GC to assess the level of precision associated with individual species measurements. The reproducibility of N_2 and CO was within one percent and CO_2 , CH_4 and C_2H_6 were reproducible to within three percent. The concentrations of H_2 and H_2O are relative to themselves only as

calibrations were not obtained. The gas analysis measurements are discussed in more detail in Reference 9.

Temperatures were determined using a fine-wire thermocouple with a 180 μm bead size. These were made by butt fusing 75 μm diameter platinum and platinum/13 percent rhodium. Temperature profiles were obtained by stretching a 20 mm length of wire parallel to the polymer surfaces along an isotherm. The distance between the thermocouple bead and surface was determined optically using a He/Ne laser light source and focusing a magnified image of the flame zone on a screen.

EXPERIMENTAL RESULTS

Composition profiles for the combustion of high purity poly(ethylene) polymer in the opposed flow of a gaseous oxygen/nitrogen stream were obtained with the objective of examining the flame structure near extinction and of checking the similarity of the reacting flow in the radial direction. Four of the experimental cases studied are reported here as illustrative examples, Table I. Cases A, B and D show the effect of decreasing oxygen mole fraction, that is, approach to extinction. Cases B and C allow examination for radial similarity, that is, invariance in the composition and temperature profiles in the radial direction. The vertical location of the probe was referenced to the polymer surface and the luminous flame zone determined visually by noting the probe location at which the probe was in the luminous flame zone. The flame stand-off distance is defined here as the distance between the peak temperature location and polymer surface. The data indicate that flame stand-off distance varies directly with oxygen concentration.

The various profiles measured are illustrated in Figs. 4-7. The radial location is given by the ratio of the radial distance to the sample radius, $r^* = r/R$. Pyrolysis products, low molecular weight hydrocarbons, are found close to the fuel surface. The dominant feature of the profiles is their marked departure from the flame sheet approximation. The penetration of O_2 into the fuel side of the flame was noted for all cases. Carbon monoxide levels at the flame are approximately an order of magnitude above equilibrium values and the ratio of measured CO to equilibrium CO increases as extinction is approached. The thickness of the luminous flame zone also increases with oxygen concentration.

Table I. Experimental conditions and results for the burning of poly(ethylene) polymer. Nozzle velocity, 0.48 m/sec; reactant temperature, 295 K; reactant pressure, 1 atm.

CASE	NOZZLE OXYGEN MOLE FRACTION ^a	RADIAL LOCATION (r/R)	PEAK TEMPERATURE (K)	FLAME STAND- OFF DISTANCE (mm)
A	0.212	0.31	1720	1.36
B	0.232	0.31	1860	1.48
C	0.232	0.67	1840	1.57
D	0.253	0.31	1960	1.70

^aRemainder of the flow is nitrogen.

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Figure 4. Composition profiles for low oxygen concentration in the oxidizer, Case A, ($X_{\text{O}_2} = 0.212$ and $r^* = 0.31$).

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Figure 5. Composition profiles for an intermediate oxygen concentration in the oxidizer, Case B, ($X_{O_2} = 0.232$ and $r^* = 0.31$).

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Figure 6. Composition profiles for a large radial position, Case C, ($X_{O_2} = 0.232$, $r^* = 0.67$).

XBL798-6731

Figure 7. Composition profiles for a high oxygen concentration in the oxidizer flow, Case D, ($X_{O_2} = 0.253$, $r^* = 0.31$).

Comparison of Figs. 5 and 6 reveals that the composition profiles are, within experimental uncertainty, identical for flames sampled at different radial sampling locations.

Temperature and equivalence ratio profiles are shown in Figs. 8-10. The peak temperature reported in Table I falls within the luminous flame zone. The peak temperature increases with initial oxygen concentration. The calculated temperature profiles shown in the figures were based on the collapsed flame zone model of the OFDF of Kenoshita *et al.*,⁵ and were determined employing their computational code. The flame stand-off distance for Case A was used to determine the velocity gradient requisite for the calculation so coincidence of the location of the predicted and measured peak temperature location for this case results from fitting rather than prediction. It is important to note that this fitting procedure scales the abscissa for the computed profiles. Both the calculated and measured peak temperature locations move toward the surface as the oxygen concentration is reduced. The local equivalence ratio was determined from the measured concentration of carbon containing species and assumes that the local hydrogen to carbon atom ratio is a constant, two, corresponding to that of poly(ethylene). The equivalence ratio at the flame is approximately one; and the position of unit equivalence ratio is nearly coincident with the location of the peak temperature. It is of interest to note that the equivalence ratio profile increases gradually on the fuel side and decreases gradually on the oxidizer side. This is inconsistent with the flame sheet model of diffusion flames where equivalence ratio is not defined on the fuel side and vanishes on the oxidizer side.

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Figure 8. Measured and calculated temperature profiles and measured equivalence ratio, Case A, ($X_{O_2} = 0.212$ and $r^* = 0.31$).

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Figure 9. Measured and calculated temperature profiles, Cases B and C, and measured equivalence ratio, Case B ($X_{O_2} = 0.232$), showing radial similarity.

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Figure 10. Measured and calculated temperature profiles and measured equivalence ratio, Case D, ($X_{O_2} = 0.253$ and $r^* = 0.31$).

DISCUSSION

Departures from the collapsed flame model are manifested by the presence of CO concentrations in excess of equilibrium values and oxygen on the fuel side of the flame. The CO concentrations at the luminous flame zone is approximately an order of magnitude greater than the computed equilibrium value. Carbon monoxide concentrations at the flame zone and on the oxidizer side of the flame in excess of equilibrium values have also been observed by other investigators.^{2,3,4,12} The final conversion of CO to CO₂ probably occurs at the edges of the OFDF at a radial location where fuel no longer flows to the flame. This is consistent with the measurements of Pandya and Weinberg¹ in a gas/gas OFDF. Penetration of oxygen to the fuel side of the flame and possibly to the polymer surface is of particular significance and is discussed later.

Maček¹³ proposed that at conditions near extinction a shift from a stoichiometry producing CO₂ to one producing CO occurs. It is important to note that substantial quantities of CO are produced at the flame zone, even away from extinction conditions. A slight increase, about ten percent, in the maximum CO/CO₂ ratio measured was observed as extinction was approached. This change is not judged to represent a significant shift in stoichiometry.

The position of unit equivalence ratio appears to move toward the fuel surface as the oxygen mole fraction increases. This may be a result of improperly accounting for carbon containing species since an increase in soot production between the flame and surface and a failure to measure the carbon associated with the soot causes an error

in carbon concentration. The increased soot production is consistent with a promotion of fuel pyrolysis caused by the higher flame temperatures.

The flame position shifts toward the fuel surface as extinction is approached, or identically, the flame stand-off distance decreases with decreasing initial oxygen concentration. These experimental results are in agreement with the predictions of the OFDF model of Kinoshita et al.,⁵ and with the modeling calculations of Feng and T'ien.¹⁴ The flame shift toward the surface is consistent with the flame temperature decline discussed in the previous paragraph. As the flame temperature decreases, the average temperature gradient between the flame and the surface decreases, the fuel blowing velocity at the surface diminishes, and the flame moves toward the surface as observed.

Similarity of the composition profiles of a flame in a stagnation point flow is predicted theoretically, but has not been verified experimentally. Similarity is of crucial importance to modeling since in the OFDF it reduces the number of independent variables by one. Pandya and Weinberg¹ experimentally confirmed the similar nature of the temperature profiles in the OFDF by determining that isotherms are parallel to the flame. In the current study composition and temperature profiles were taken at a small radial position (Case B) and a large radial position (Case C). These profiles are similar to within the experimental uncertainty. This result supports the use of the similarity assumption for modeling studies in the opposed flow configuration.

Oxygen was found on the fuel side of the diffusion flame, a departure from the collapsed flame model, but consistent with other experimental observations of diffusion flames.^{2,3,4,12} The oxygen concentration at the luminous flame zone decreased with decreasing initial oxygen concentration; the opposite trend was reported by Seshadri and Williams⁴ in their OFDF study of methyl methacrylate. Oxygen transport to the surface is important because it can result in exothermic surface oxidation reactions and increase the fuel pyrolysis. Stuetz et al.,¹⁵ have proposed that polymer surface oxidation reactions provide significant energy for pyrolysis. The oxygen concentration gradient and oxygen concentration near the surface were examined in the current study to address this question. The difference between the oxygen diffusion rate to the surface and the rate at which oxygen is transported away from the surface by the pyrolyzing polymer was calculated. If the assumption is made that no O_2 diffuses into the polymer, any excess of diffusion inflow over convection outflow is the reaction rate of oxygen at the surface interface.

A diffusion model using Fick's Law was used with multicomponent diffusion coefficients estimated from binary diffusion coefficients based on the Lennard-Jones potential. Oxygen concentrations and gradients were evaluated using experimental data nearest the surface. It was further assumed that any oxygen disappearing at the surface forms CO_2 and H_2O and that the energy released is then used exclusively for depolymerization. Such assumptions establish an upper bound to the contribution of surface oxidation energy release to depolymerization.

The set of composition profiles that yielded the greatest net transfer of oxygen to the surface was considered (Case D). The following values were used: fuel mass flux of $6.6 \text{ g/m}^2\text{s}$ (the polymer burning rate), gradient in oxygen mole fraction of 7.4 m^{-1} , oxygen mole fraction of 5.4×10^{-3} , surface temperature of 900 K and enthalpy of depolymerization of 3.85 kJ/g. The result of this energy release calculation indicated that heterogeneous surface oxidation could provide at most twenty percent of the energy required for depolymerization. Unfortunately, the precision of the experimental measurements were not sufficient to fully answer the question of the importance of surface oxidation of the polymer as raised by Stuetz et al.¹⁵ Our results suggest that heat transfer to the surface from the flame rather than surface oxidation controls the pyrolysis, and therefore, burning rate.

CONCLUSIONS

Measurement of the composition profiles for a high purity poly(ethylene) OFDF revealed departures from the flame sheet approximation: oxygen penetrated to the fuel side and CO concentrations exceeded equilibrium values. The precision of the oxygen profile measurement was not adequate for an accurate determination of the oxygen flux to the surface; however, a maximum contribution of surface oxidation was estimated to be twenty percent of the enthalpy required for fuel pyrolysis.

As extinction was approached through reduction of the oxygen concentration in the oxidizer flow, the CO/CO₂ ratio increased slightly, oxygen concentration at the luminous flame zone decreased, the flame location moved toward the surface, the position of unit equivalence ratio moved away from the surface and the maximum flame temperature decreased.

Composition and temperature profiles are similar in the radial direction--a condition which greatly simplifies modeling of this reacting flow.

ACKNOWLEDGMENTS

This work was supported by the National Bureau of Standards, Center for Fire Research Contract No. NBS-G-7-9006 and by the U.S. Department of Energy under contract No. W-7405-ENG-48. The authors are extremely grateful to Dr. Amos Newton for his assistance in the development of the gas analysis system.

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