Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

MODELLING OF BURNING AND EXTINCTION CHARACTERISTICS
OF A POLYMER DIFFUSION FLAME AND COMPARISON WITH
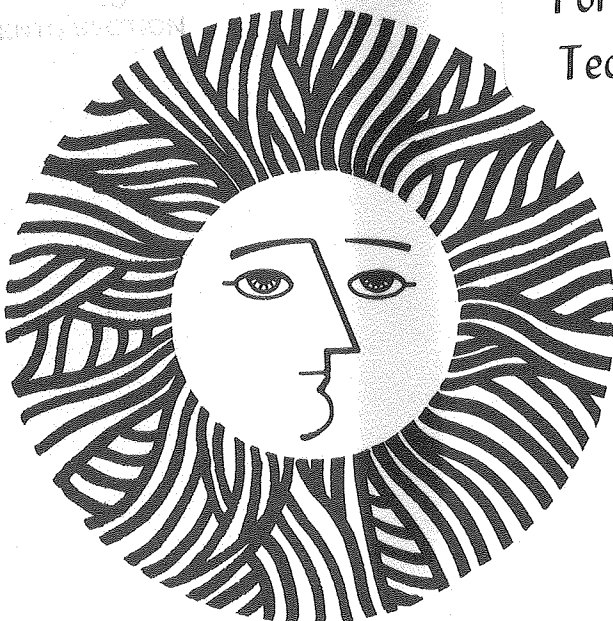EXPERIMENT

W.J. Pitz and R.F. Sawyer

April 1981

DISCLAIMER

MODELLING OF BURNING AND EXTINCTION CHARACTERISTICS OF

A POLYMER DIFFUSION FLAME AND COMPARISON WITH EXPERIMENT

W.J. Pitz and R.F. Sawyer
Department of Mechanical Engineering
University of California
Energy and Environment Division
Lawrence Berkeley Laboratory
Berkeley, California 94720 USA

INTRODUCTION

The importance and contribution of the inherrent flammability of polymeric materials to problems of fire safety is well recognized. This study was undertaken to provide a better understanding and interpretation of previous experimental investigations of polymer flammability. The structure of opposed flow diffusion flames have been measured by several investigators using both gaseous[1,2] and solid[3,4,5] fuels. The opposed flow diffusion flame is a convenient geometry for the study of the flammability of polymers because it allows both steady, diffusion controlled burning and extinction to be observed under well-controlled laboratory conditions. Conveniently available experimental parameters include fuel composition, oxidizer composition, and oxidizer blowing rate. Reported experiments generally have not included the variation of pressure or temperature. Radiation effects, which are important in fires, remain to be well-characterized in laboratory studies of opposed flow diffusion flames where radiation generally is of minor importance.

Theoretical descriptions of opposed flow diffusion flames have been provided by several investigators[6-10]. In most cases the flame sheet approximation of Burke and Schumann[11] has been invoked, generally to allow a simplified description and analytical solution. The flame structure in these models is simplified to a surface which is the locus of stoichiometric composition where an infinitely rapid reaction occurs. Experimentally we have observed that the flame zone is not thin, especially near extinction conditions, with oxidizer penetrating to the fuel side of the flame and fuel or intermediate, partially reacted fuel (primarily carbon monoxide) penetrating to the oxidizer side[5].

A previous study[5] of the steady-state burning and extinction characteristics of high purity poly(ethylene) and mixtures of nitrogen and oxygen provides experimental data on the structure of the reaction zone in terms of composition and temperature, and steady burning rate data. Fundamental data on polymer pyrolysis product properties, reaction mechanisms, and reaction rates are not available and had to be approximated from earlier experiments or chosen to provide a fit between the model and experimental observations.

FORMULATION

Reacting flow in a stagnation point boundary layer was modelled with the objective of examining its properties near extinction, Fig. 1. Axi-symmetric geometry, laminar-flow and steady-state combustion were considered to conform to an existing diffusion flame burner[5]. Variation of fluid properties with both temperature and composition was included. The specific heats of the three species considered, fuel, oxygen and products were chosen to be those of ethylene, oxygen and nitrogen respectively, and approximated as cubic functions of temperature. The effective viscosity was obtained from the individual, temperature-dependent viscosities using Wilke's mixture rule[12]. The Prandtl number was fixed at 0.7, which is a good approximation for the reactants and products considered. The Lewis number was assumed to be 1.

Finite reaction rate chemistry was incorporated with a one-step reaction and Arrhenius rate expression. Three species were considered: fuel, oxygen and products. The reaction rate was of order one with respect to both fuel and oxygen.

The boundary conditions for the N_2/O_2 flow were an ambient
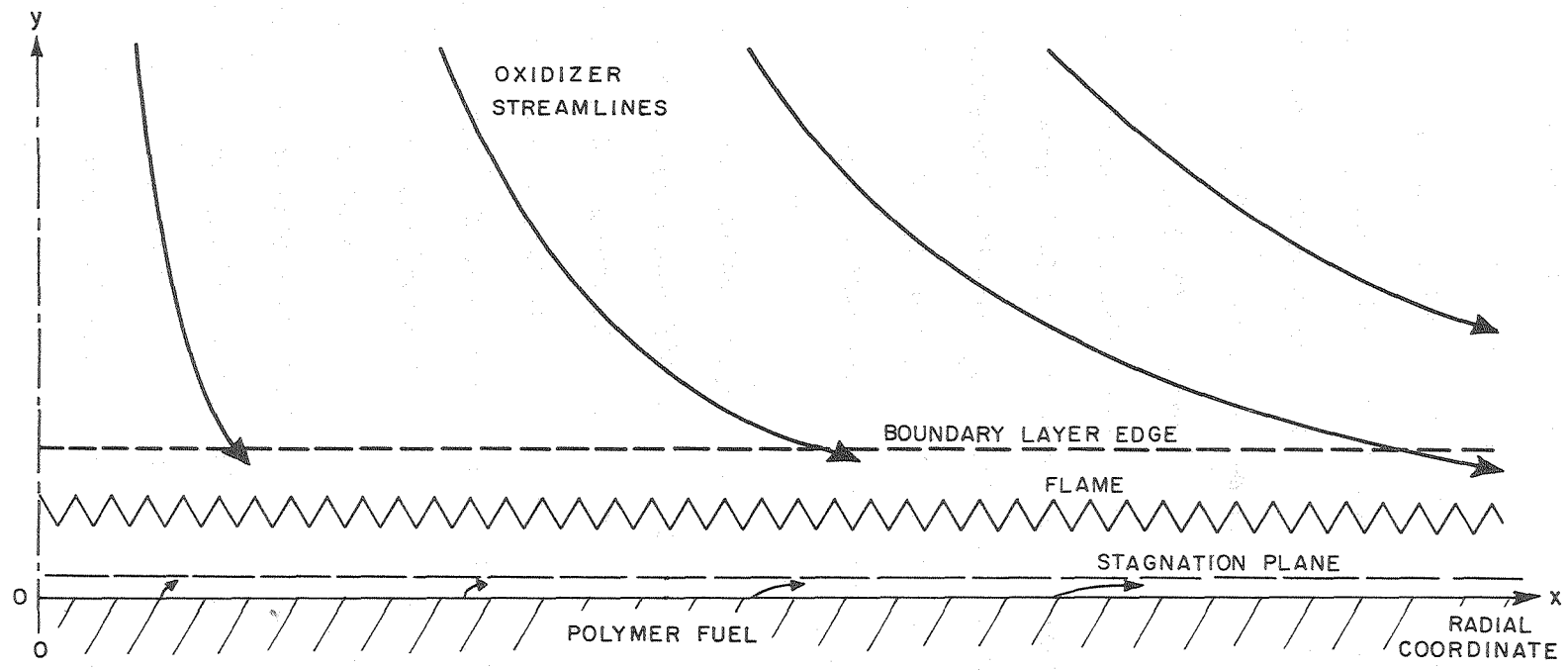
Figure 1. Description of a reacting, stagnation-point flow.

XBL 811-5106

temperature of 294K and pressure of 1 atm. The polymer burning rate
was calculated from the enthalpy gradient at the fuel surface and the
effective latent heat. The latent heat was extracted from the mass
transfer B number, previously reported by Holve and Sawyer[8] based on
their experimental observation of the combustion poly(ethylene) in an
opposed flow diffusion flame, $B = 3.48Y_0\infty - 0.18$, where $Y_0\infty$ is the
oxygen mass fraction in the ambient N_2/O_2 flow. The fuel surface
temperature was specified at 800K, also based on experimental observa-
tion[8]. The oxygen concentration at the fuel surface was set at zero.
The fuel surface mass fraction, Y_{fw}, results from species and energy
balances, $Y_{fw} = (B - Y_0\infty/s)/(1 + B)$ (Eq. 1), where s is the stoichio-
metric ratio, mass fuel consumed per mass of oxygen[7].

RESULTS AND DISCUSSION

Solutions to the boundary layer equations were found by using
GENMIX[13], which solves the finite difference equations in implicit form.
The flame structure was found for both finite and infinite reaction
rate cases for an oxygen mass fraction, $Y_0\infty$, of 0.257 as shown in Figs.
2 and 3. If only a solid curve appears on the profiles, the finite and
infinite reaction-rate curves are superimposed for this graph size. For
an infinite reaction rate, the oxygen and fuel concentrations go to zero
at the maximum temperature location which will be designated the flame.
When the reaction rate is finite, some of the fuel and oxygen survive
and are transferred through the flame. Transfer of molecular oxygen through
the flame was also found experimentally[5] as shown by the experimental
points in Fig. 2.

Calculated temperature profiles for finite and infinite reaction rates
and a measured temperature profile are presented in Fig. 3. The maximum
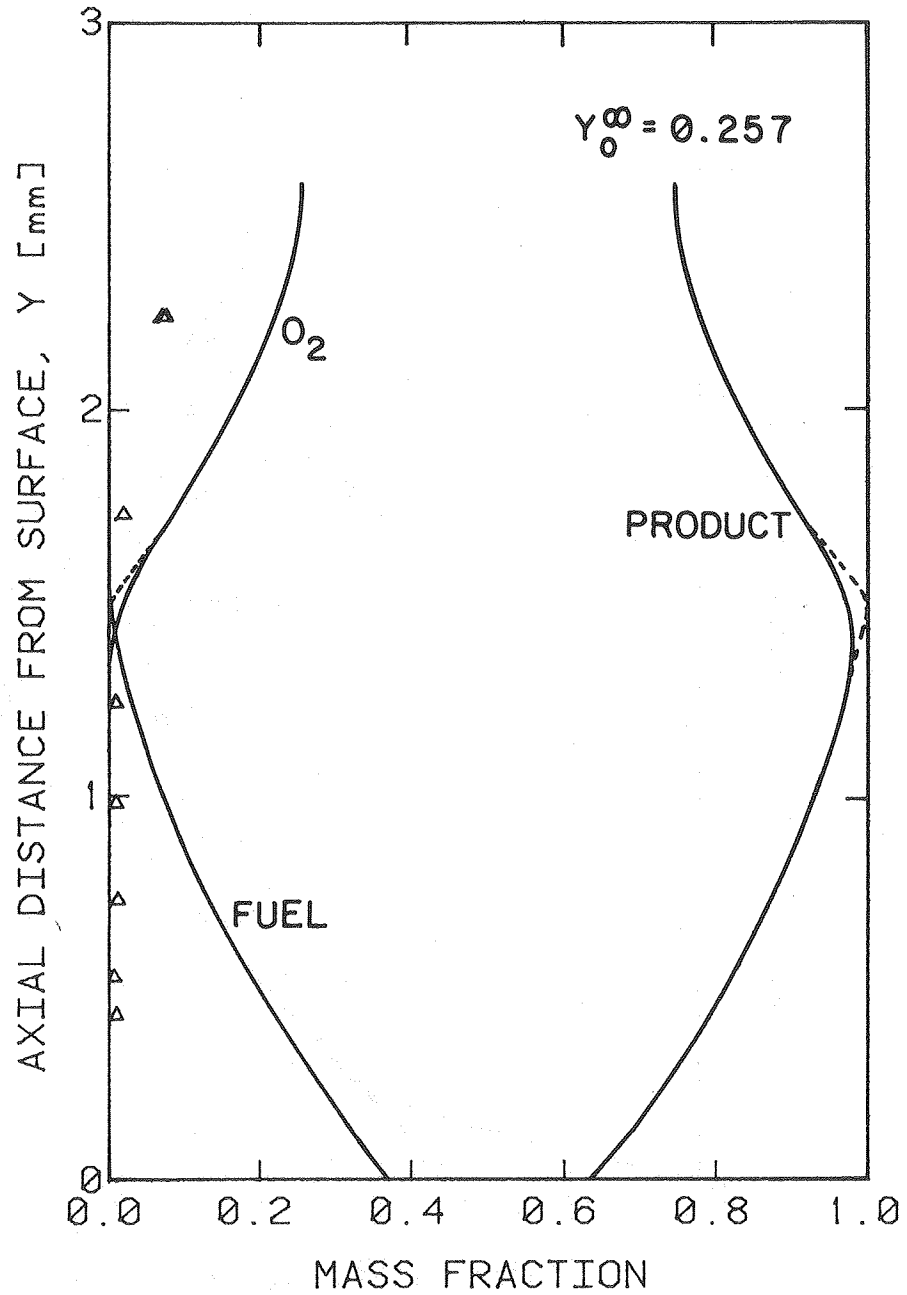
Figure 2. Calculated species profiles for finite (—) and infinite (---) reaction rates. Measured oxygen profile (Δ).
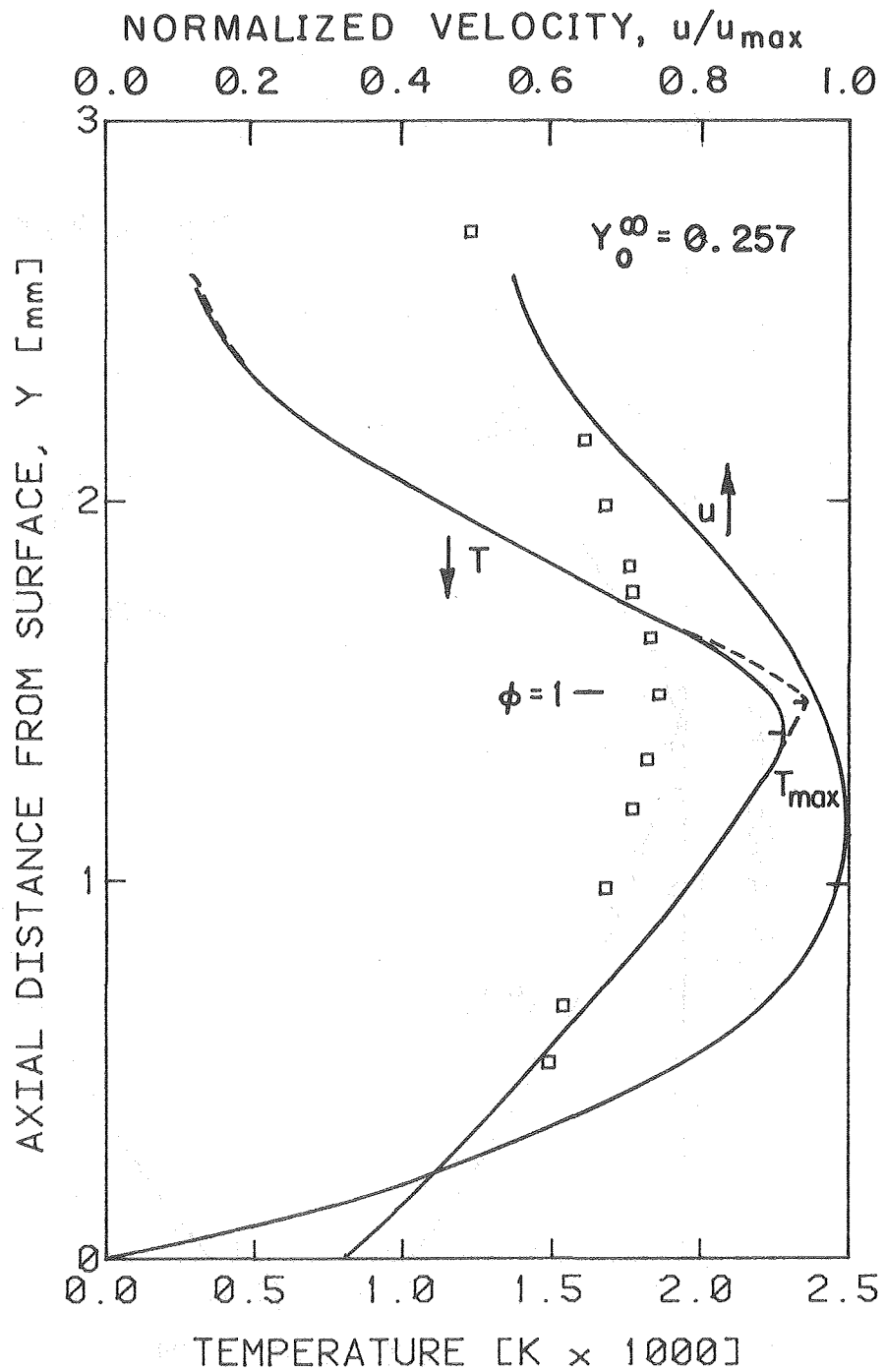
Figure 3. Calculated temperature profiles for finite (——)
and infinite (---) reaction rates. Measured
temperature profile (□). Calculated velocity
profile.

temperature for the infinite rate case was adjusted to be the adiabatic equilibrium temperature by choice a multiplicative constant in the product specific heat. The maximum temperature for the infinite rate case is higher than the finite rate case. When the reaction rate is finite, heat transfer from the flame has time to occur, and the flame cools. Both calculated temperatures were higher than the measured temperatures taken in the opposed flow apparatus[5]. A thermocouple bead of 0.18mm diameter was used in the measurements. Its characteristic measurement volume resulted in some smoothing of the peak in the temperature profile. Additionally, the temperatures were reported without correction for radiation losses.

In comparing infinite to finite reaction rate cases, the flame temperature drops and the flame moves closer to the surface, Fig. 3. The surface temperature gradient and thus the burning rate, however, is unchanged. The calculated burning rate is 29 g/m^2s whereas the measured value is 8.3 g/m^2s. This discrepancy could have resulted from the calculated flame temperatures being too high and a failure to consider surface radiation loss in the model. The peak temperature from measurement and the calculated peak temperature from the infinite rate case are at the same location which is a result of fitting rather than prediction. The peak temperature location in the measured profile was used to determine the velocity gradient at the boundary layer edge which is requisite for the calculation. The location of unity equivalence ratio, frequently used to denote the flame location, is the same for both the finite and infinite rate cases.

The calculated boundary layer thickness for temperature is less than the measured one, Fig. 3. The actual flame thickness is probably greater

than that predicted by a one-step, finite rate reaction. The inclusion of
complex flame chemistry would spread out the flame. For one-step chemistry,
all the chemical reaction occurs very near the maximum temperature location.
For an actual diffusion flame, fuel pyrolysis reactions occur near the
surface, H_2O formation occurs near the peak temperatures, and CO_2 formation
occurs on the oxidant side of the flame[2].

The velocity profiles for the finite and infinite reaction rate are
identical on the graphic scale presented. The variable u/u_{max} is plotted
since it is independent of radial location. The location of u_{max} is between
the flame and fuel surface for the following reasons. Since the viscosity
is temperature dependent, it is maximum at the flame. As indicated in Fig.
1, the streamlines pass through the flame convecting the flow into the lower
viscosity region where the maximum velocity is attained.

Calculated flame stand-off distances for finite and infinite reaction
rates and measured stand-off distances are shown in Fig. 4. All flame
stand-off distances presented decrease with decreasing ambient oxygen mole
fraction, $X_0\infty$. When $X_0\infty$ is lowered, the flame temperature is reduced,
which decreases temperature gradient at the surface and thereby the fuel
blowing rate. The fuel mass fraction at the surface is also decreased
since the B number is lowered, Eq. 1. Both of these effects reduce the
flame stand-off distance. It is crucial to include finite rate flame
chemistry when predicting flame stand-off distances near extinction, Fig.
4. When $X_0\infty$ is increased, the flame condition moves out of the extinction
regime and the flame stand-off distance predictions are the same for both
finite and infinite rate cases. If the flame is near extinction, the
net fluid motion through the flame and towards the surface becomes important.
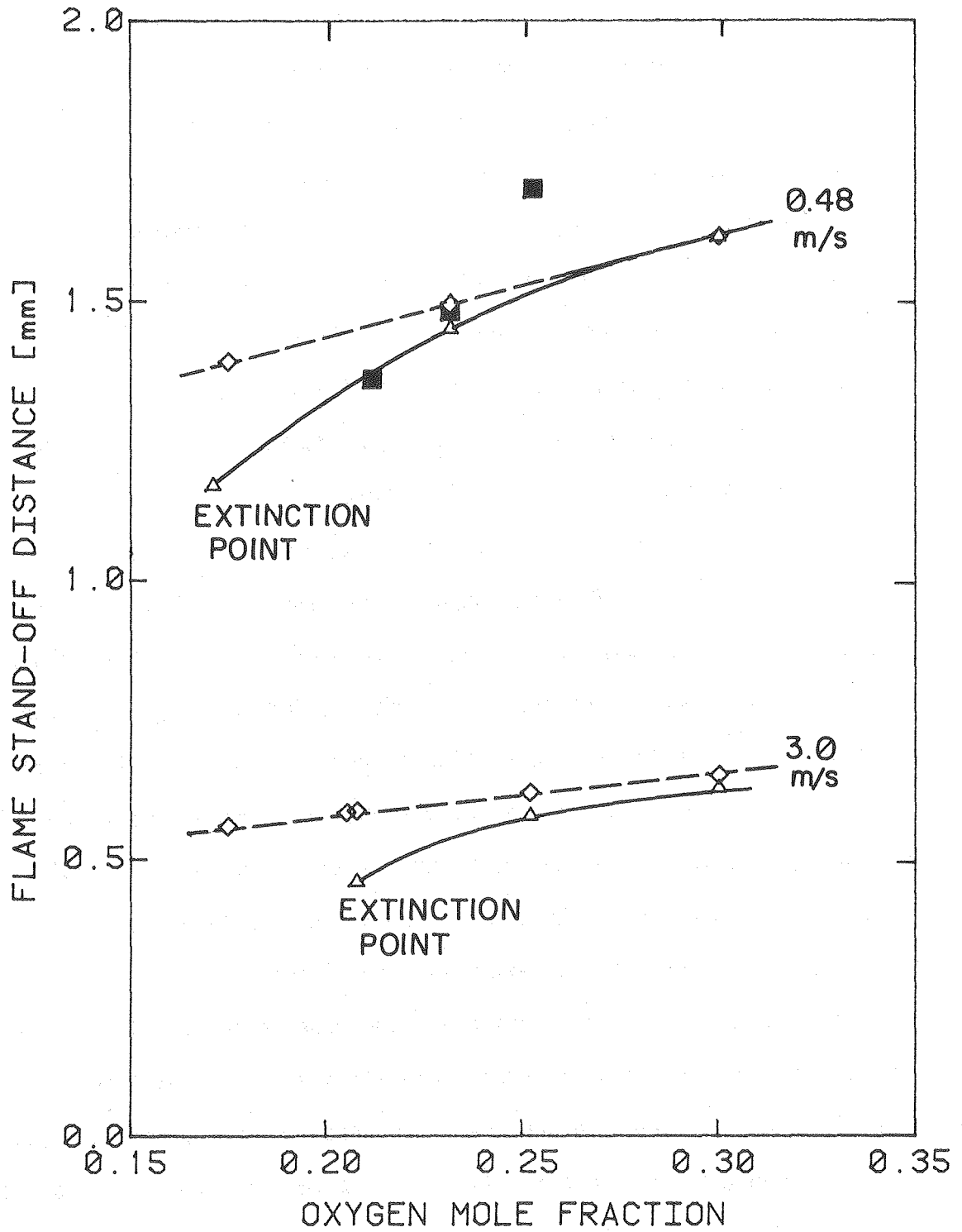
Figure 4. Flame stand-off distance calculated for finite (—) and infinite
(---) reaction rate and measured by experiment (■).

XBL811-5111

The reactants are convected for significant distance before they are fully reacted and the maximum temperature is reached.

Overall reaction-rate parameters were extracted from extinction data. Extinction measurements in the opposed flow apparatus were performed for poly(ethylene) burning in N_2/O_2 mixtures, Fig. 5. The values of the reaction-rate parameters were iterated until the calculated extinction curve approximated the least squares fit of the data. The resultant activation energy, E_A, and pre-exponential coefficient, K, are defined by the following Arrhenius expression, $\dot{m}_f = K\ p^2\ Y_f\ Y_0\ exp\ (-E_A/RT)$, where E_A is 31 ± 3 kcal/gmole, K is 5.4 x 10^{-2} kg/(Pa)^{2}m^{3}s, $\dot{m}_f$ is the mass consumption rate of fuel per unit volume in kg/m^{3}s, p is the pressure in Pa, Y_f and Y_0 are the fuel and oxygen mass fractions, R is the gas constant and T is the temperature in K. These overall rate constants were found for flame temperatures less than 1850K as indicated by calculated temperatures. The extinction condition is very sensitive to the value of $X_{0\infty}$. The flame is in a large activation energy regime where the reaction rate is mainly controlled by the flame temperature. A small change in $X_{0\infty}$ alters the flame temperature which significantly affects the reaction rate and thus the extinction condition.

The flame temperature at extinction increases slightly with nozzle velocity, Fig. 6. For higher nozzle velocities a faster reaction rate is required for the flame to survive. The reaction rate from the calculated activation energy is a strong function of temperature. Therefore, a slight increase in flame temperature was sufficient to accomodate the higher nozzle velocities. The calculated flame temperatures at extinction are lower than the infinite-rate temperatures. The infinite-rate temperatures
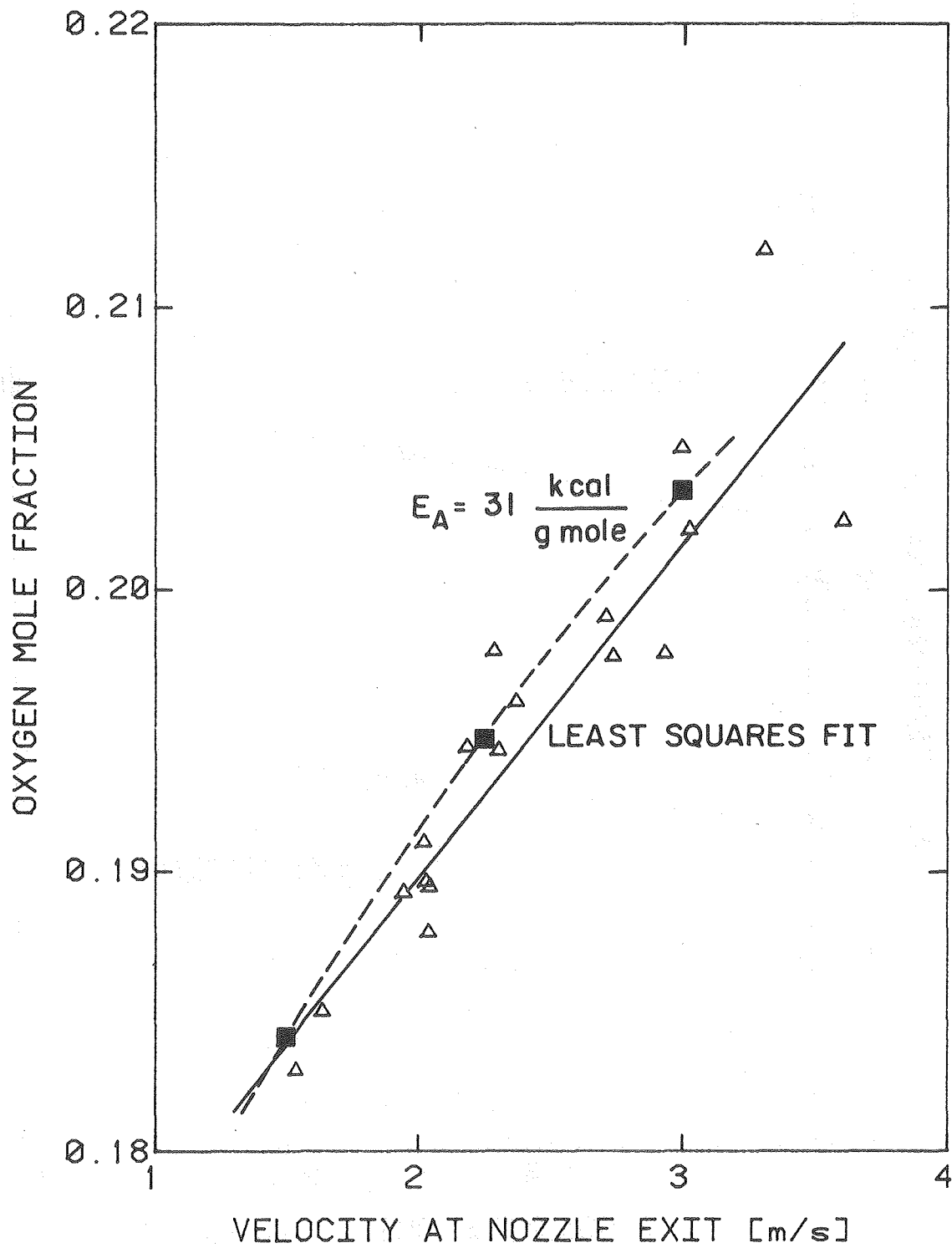
XBL 811-5113

Figure 5. Measured extinction conditions for PE burning in N_2/O_2 mixtures ($\triangle$) and calculated extinction conditions ($\blacksquare$).
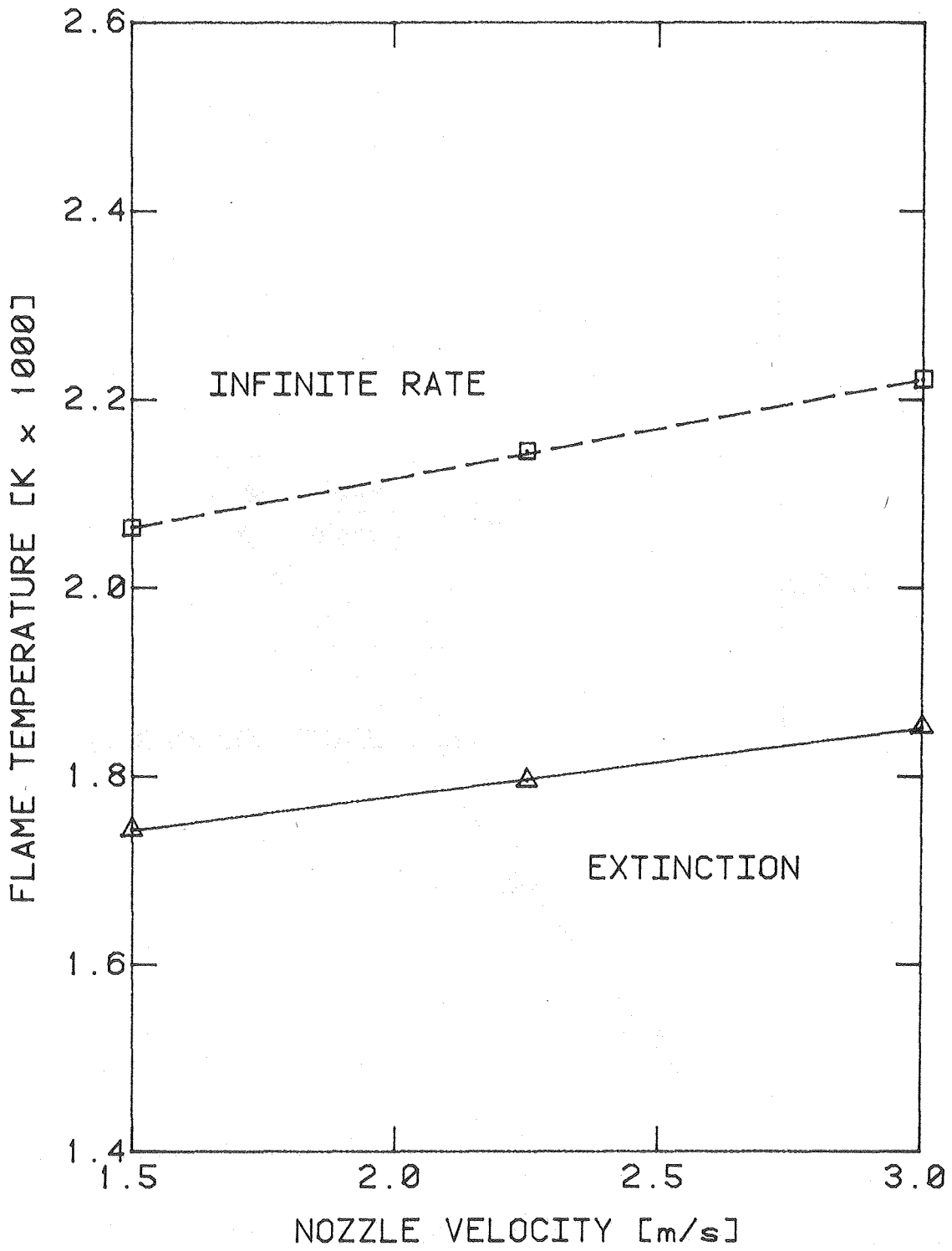
Figure 6. Calculated flame temperatures for infinite
           rate (---) and extinction (—).

XBL 814-9336

are the adiabatic flame temperatures. At extinction, the calculations indicated about a 16% reduction in flame temperature from the infinite reaction rate value.

CONCLUSIONS

1. The applicability of a boundary layer solution with a finite reaction rate to model the opposed flow diffusion flame combustion of poly(ethylene) has been demonstrated. Penetration of oxygen through the flame is predicted, in agreement with experimental observation.

2. The prediction of flame stand-off distance near extinction requires consideration of finite rate chemistry.

3. A global reaction rate for poly(ethylene) combustion in a diffusion flame was obtained through fitting extinction data to the model. The activation energy is 31 ± 3 kcal/gmole and the pre-exponential coefficient is 5.4×10^{-2} kg/(Pa)^{2}m^{3}s.

4. The maximum radial velocity occurs between the flame and the surface.

REFERENCES

1. Pandya, T. P. and Weinberg, F.J.: Proc. Roy. Soc. A, 279, 544, 1965.

2. Tsuji, H. and Yamaoka, I.: Twelfth Symposium (International) on Combustion, p. 997, The Combustion Institute, 1969.

3. Richard, J.R., Vovelle, C. and Delbourgo, R.: Fifteenth Symposium (International) on Combustion, p. 205, The Combustion Institute, 1975.

4. Seshadri, K. and Williams, F.A.: J. Polymer Sci.: Polymer Che. Ed., 16, 1755, 1978.

5. Pitz, W.J., Brown, N.J. and Sawyer, R.F.: Eighteenth Symposium (International) on Combustion, The Combustion Institute, 1981.

6. Krishnamurthy, L. and Williams, F.A.: Acta Astronautica, 1, 771, 1974.

7. Kinoshita, C.M., Pagni, P.J., and Beier, R.A.: Eighteenth Symposium (International) on Combustion, The Combustion Institute, 1981.

8. Holve, D.J. and Sawyer, R.F.: Fifteenth Symposium (International) on Combustion, p. 351, The Combustion Institute, 1975.

9. Krishnamurthy, L., Williams, F.A., and Seshadri, K.: Combustion and Flame, 26, 363, 1976.

10. T'ien, J.S., Singhal, S.N., Harold, D.P. and Prahl, J.M.: Combustion and Flame 33, 55, 1978.

11. Burke, S.P. and Schumann, T.E.W.: Ind. Eng. Chem. 20, 988, 1928.

12. Wilke, C.R.: J. Chem. Phys. 18, 517, 1950.

13. Spalding, D.B.: GENMIX: A General Computer Program for Two-Dimensional Parabolic Phenomena, Pergamon Press, 1977.