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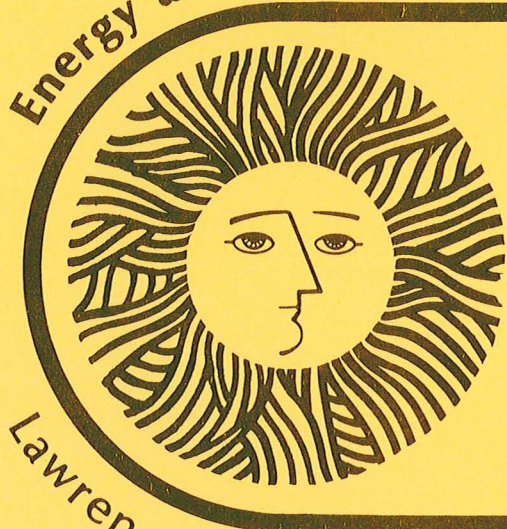
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Inhibition Effects On Extinction
Of Polymer Burning

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INHIBITION EFFECTS ON EXTINCTION OF POLYMER BURNING*

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ABSTRACT

The opposed flow diffusion flame has proven a useful laboratory tool for the study of the combustion of both liquids and solids. Quantitative determinations of burning rates, extinction limits, mass transfer numbers, solid fuel thermal diffusivities, and flame structures have been obtained under well-controlled and reproducible conditions, Holve and Sawyer (1975), T'ien, et al. (1976). Extinction limits are of particular interest, especially in assessing inhibitor addition. Extinction data reveal the effect of inhibitors on the chemical reaction rate. In this study inhibitors have been added to both the gaseous oxidizer and the solid fuel.

Extinction data have been obtained for polyethylene (PE) and poly(vinyl chloride) (PVC) in N_2/O_2 mixtures. These data are compared to extinction measurements of polyethylene with an $N_2/O_2/HCl$ mixture. Poly(vinyl chloride) differs chemically from polyethylene only by a substitution of a chlorine atom for a hydrogen atom in the monomer. With the inclusion of this halogen atom, poly(vinyl chloride) may be thought of as an "inhibited" polyethylene and therefore well suited for a comparative study.

The behavior of the HCl added to the oxidizer side of the diffusion flame was found to be primarily that of an inert, in comparison to Cl being added to the fuel side of PVC. Impurities in this commercial PVC and PE may have had an effect on the extinction data.

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INTRODUCTION

Of present interest are polymers, long chain molecules which include plastics as the largest subgroup. Because polymers have many practical applications and are used widely, investigation of their hazards is appropriate. Most polymers in their pure form are dangerously flammable since their primary constituents, carbon and hydrogen, are readily oxidized.

Fire hazards of polymers can be greatly reduced by the addition of fire retardants. Halogens, such as bromine and chlorine, are an important class of retardants commonly added to polymers. This work is part of a larger study to determine the mechanism of halogen inhibition in polymers.

Two important mechanisms of retardancy are chemical inhibition of exothermic reactions and the promotion of charring. Charring is the production of a high carbon content layer at the surface of a burning polymer. The char layer impedes heat transfer to the polymer, slowing pyrolysis and vaporization. Consequently, combustion is slowed. Chemical inhibition occurs predominantly in the gas phase by interfering with the flame kinetics. Halogens, for example, are chemical inhibitors that are thought to scavenge radicals in the flame zone (Fristrom, 1967). Radicals which promote chain branching are partially nullified and thus the overall reaction rate is lowered. This study is focused on halogen inhibitors.

If one can determine under what conditions halogens are effective or ineffective inhibitors, insight into the mechanism of their behavior should result. In this experiment, an attempt is made to determine if

the halogen Cl is more effective when introduced with the oxidizer or with the fuel.

Creitz (1961) added inhibitors to the fuel and oxygen side of a Burke-Schumann (1928) diffusion flame. CH_3Br and CF_3Br were found to be much more effective when added to the oxygen side of the reaction zone of a hydrogen or gaseous hydrocarbon flame than when added to the fuel side. Ibirica and Gaydon (1964) mixed halogen inhibitors with both the fuel and oxidizer of hydrogen, methane, and ethylene diffusion flames. Emission spectra for their opposed flow diffusion flame were recorded, but no extinction measurements were made. Kent and Williams (1975) added CF_3Br to the oxidizer in an opposed flow experiment using liquid heptane as a fuel. They obtained composition profiles and extinction data, but did not investigate the case of inhibitor addition to the fuel.

In premixed flames, halogen inhibitors lower the reaction rate and flame speed. Halogen inhibitors have only a slight effect on burning rates of diffusion flames since such flames are diffusion and not chemically controlled. In a gas phase diffusion flame the inhibitor effectiveness can be assessed by conditions at blowout since a balance between reaction rate and transport occurs. One reduces the flow time of the reactants in the flame zone until the reactants have insufficient time to react. Extinction or blowout is one of the fundamental characteristics of a diffusion flame. The critical parameter is Damköhler's first group:

$$D_{a_I} = \tau_F / \tau_R \lesssim 1 \quad (\text{for extinction})$$

where τ_R is the characteristic reaction time and τ_F is the characteristic flow time. When the flow time is decreased until the Damköhler number is below a critical value on the order of one, extinction results. Consequently, a flow time at extinction is proportional to the overall

reaction time. The characteristic reaction time suggests inhibitor effectiveness. Therefore, inhibitor effectiveness in this study was determined from extinction experiments.

EXPERIMENTAL CONFIGURATION

The opposed flow diffusion flame apparatus (Figures 1 and 2) was used to determine extinction conditions for polymers. Of the many configurations for diffusion flames that have been considered, the opposed flow exhibits steady state burning (Holve and Sawyer, 1975) and provides a convenient tool for studies of polymer burning. A laser feedback control system maintains a steady fuel surface location. Polymer dripping and fuel surface deformation that complicate analysis in other commonly used polymer combustion experiments are not found here. For the polymers considered, polyethylene and poly(vinyl chloride), and the flow range studied, the resulting flame is axisymmetric, somewhat rounded, and lies slightly (about 1 mm) above the surface of the polymer.

Extinction was obtained in these experiments by increasing the oxidizer flow until the entire flame blew out. An alternative method is to define extinction as occurring when the flame is extinguished in the center only but, not at the perimeter. As the flowrate is increased the opposed flow flame usually extinguishes at the center first and then proceeds radially outward.

METHOD OF INHIBITOR ADDITION

Insight into chlorine's behavior should be gained by determining in which region of the diffusion flame it is the most effective inhibitor. For this study, chlorine was introduced as HCl in the oxidizer and compared to chlorine added to the fuel side (as poly(vinyl chloride)).

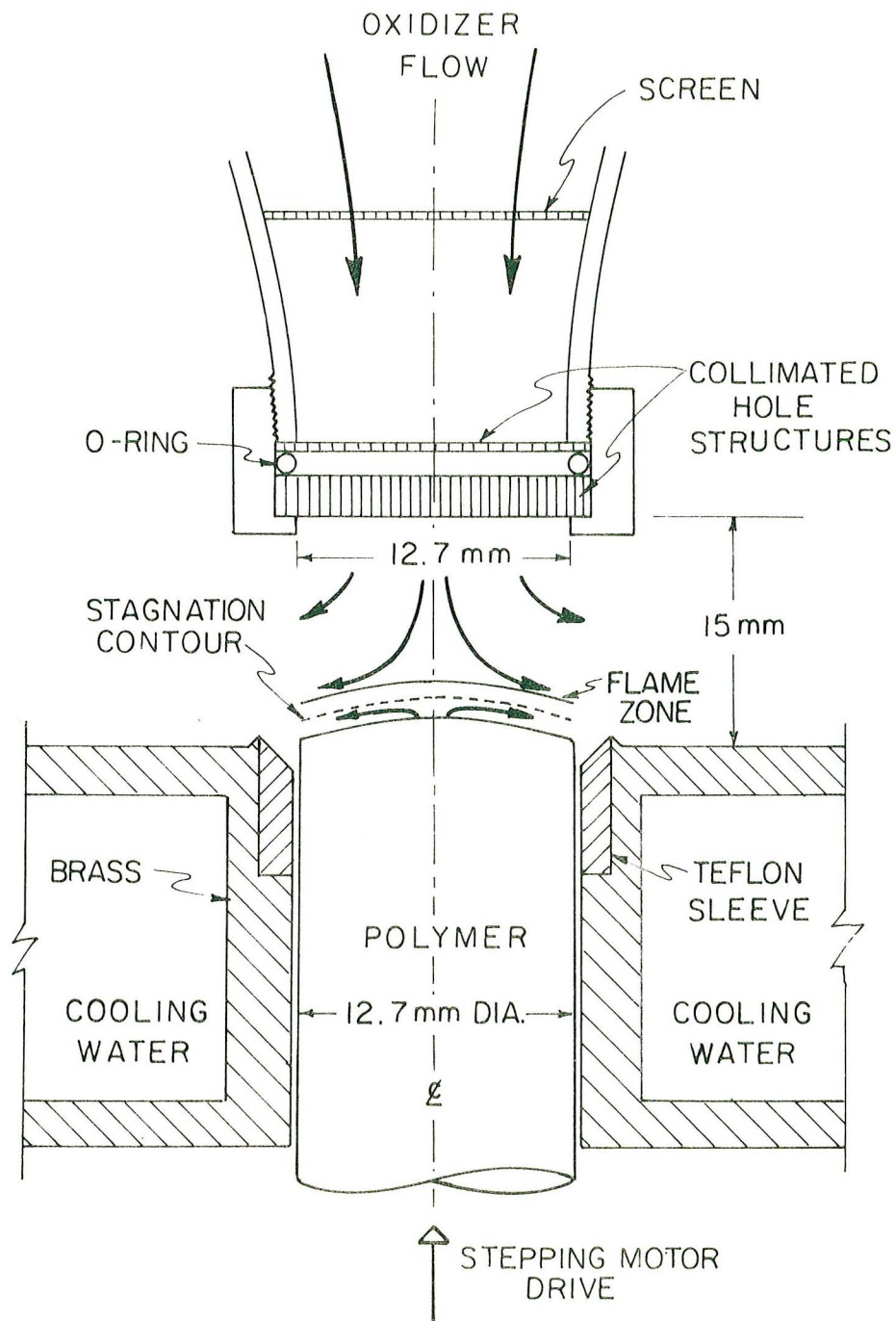


Figure 1. The opposed flow diffusion flame configuration.

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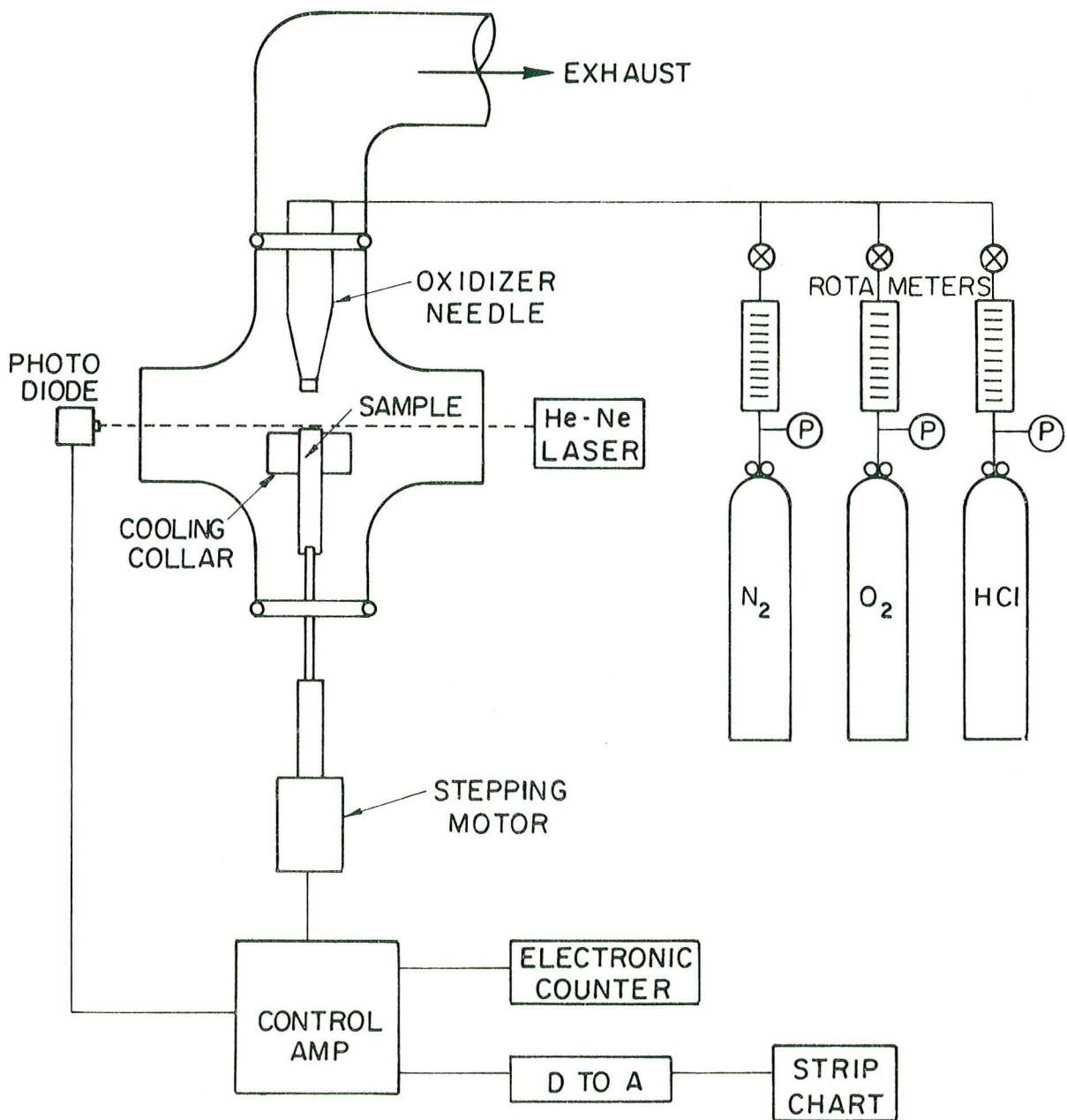
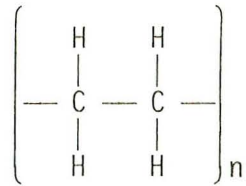


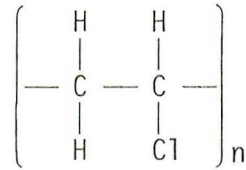
Figure 2. The opposed flow diffusion flame experimental setup.

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The polymer used in the HCl case was polyethylene (PE) which differs in chemical structure from poly(vinyl chloride) (PVC) by an H atom substituted for a Cl atom:



Polyethylene
PE



Poly(vinyl chloride)
PVC

Differences in thermochemical properties are shown in Table 1. For these studies, commercial PVC and low molecular weight PE were used which commonly contain silicon, lead, and antimony as impurities (Schacke, et al., 1976). In future studies, pure samples will be used.

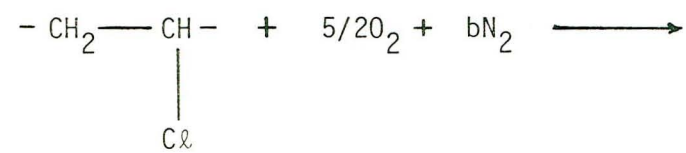
HCl was chosen as a model inhibitor for oxidizer side addition since it is one of the simplest chlorine inhibitors chemically and it is a likely pyrolysis product of PVC (O'Mara, et al., 1973). PVC was chosen to represent fuel side addition of chlorine since it is chlorine substituted PE. A contribution to the understanding of inhibition in PVC and PE would be beneficial since they are both widely used commercial polymers.

To compare the addition of chlorine to the oxidizer with addition to the fuel, one must decide on the appropriate amount of HCl. The overall combustion reactions for PE and PVC are given in Table 2. For each $\text{C}_2\text{H}_3\text{Cl}$ of PVC burned, one Cl atom is introduced into the flame zone. Referring to the PE reaction, in order to introduce one Cl atom for each C_2H_4 of PE burned, the ratio of moles HCl to moles O_2 would have to be 1/3:

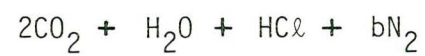
Table 1.
 PROPERTIES OF POLYETHYLENE AND POLY(VINYL CHLORIDE)*

	<u>Polyethylene</u>	<u>Poly(vinyl chloride)</u>
Enthalpy of Formation (298 K)	-53.5 MJ/kg-mole	-94.6 MJ/kg-mole
Enthalpy of Combustion (298 K)	-1310 MJ/kg-mole	-1120 MJ/kg-mole
Adiabatic Flame Temperature ($\phi=1$, air)	2393 K	2233 K
Chemical Structure	$\left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C} - \text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right)_n$	$\left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C} - \text{C}- \\ \quad \\ \text{H} \quad \text{Cl} \end{array} \right)_n$

*Throne and Griskey, 1972.



Polyvinyl chloride



Polyethylene

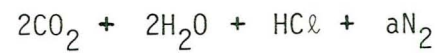


Table 2. Overall Combustion Reactions of PVC and PE.

$$\frac{\eta_{\text{HCl}}}{\eta_{\text{O}_2}} = \frac{1}{3}$$

Accordingly, the extinction curves were obtained for PVC in an N_2/O_2 mixture and PE in an $\text{N}_2/\text{O}_2/\text{HCl}$ mixture where $\eta_{\text{HCl}}/\eta_{\text{O}_2} = 1/3$.

EXTINCTION CURVES

A typical extinction curve is shown in Figure 3 for PVC and PE with no HCl. The nozzle exit velocity is plotted as the independent variable since it controls the flow time in the reaction zone. As shown in Figure 1 the stagnation contour lies below the flame zone (Holve and Sawyer, 1975; Kent and Williams, 1975) so the nozzle velocity rather than the fuel blowing velocity regulates the mass average velocity in the flame zone.

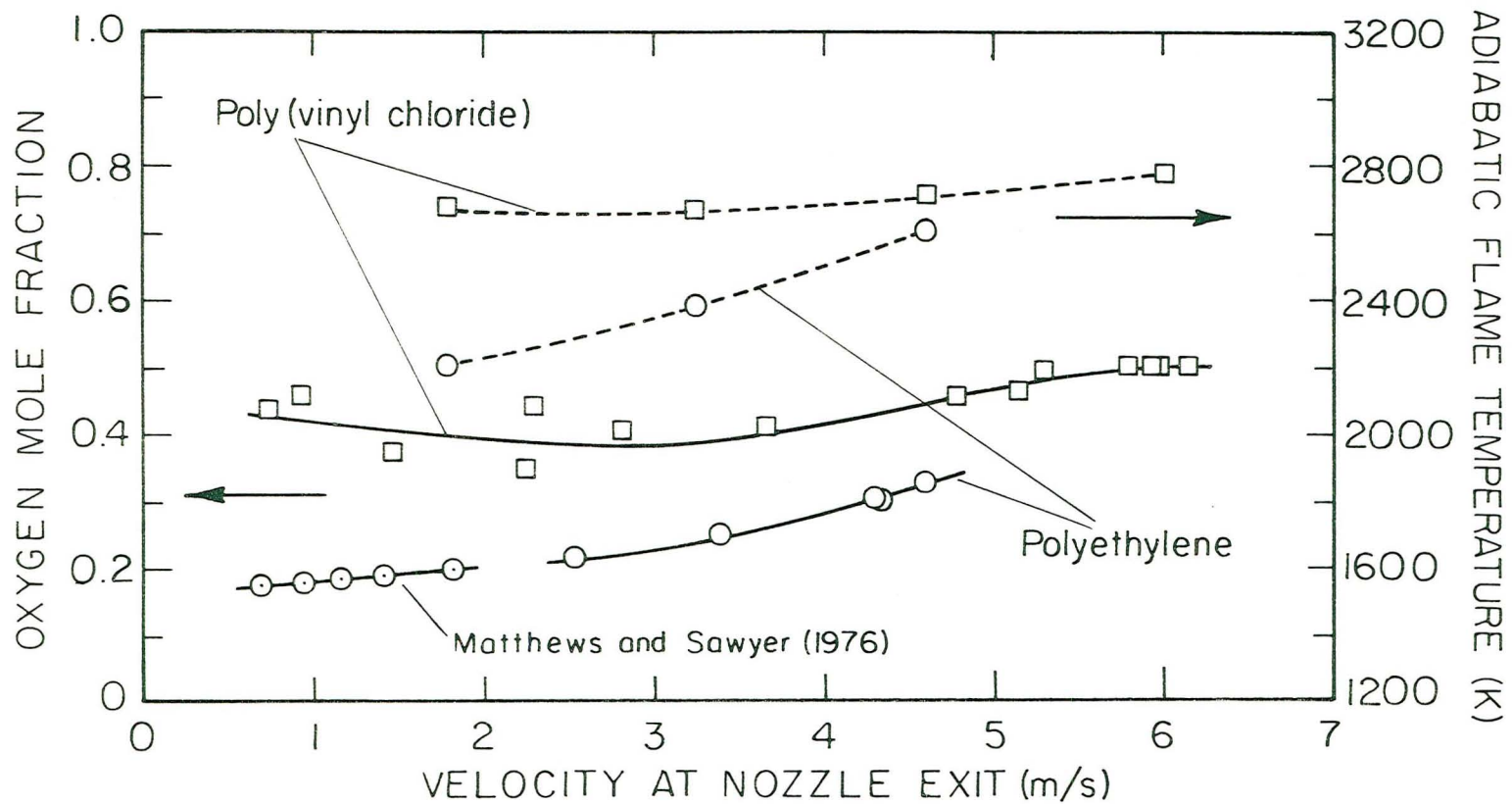
The oxygen mole fraction X_{O_2} is plotted since it partially regulates the reaction time in the flame zone. This can be seen by considering the rate of reaction R,

$$R \sim k X_{\text{O}_2}^a X_f^b$$

where the k is the rate constant; X_f is the mole fraction of the fuel; a and b are the orders of the reaction. So for the characteristic reaction time τ_R ,

$$\tau_R \left(\sim \frac{1}{R} \right) = \tau_R(X_{\text{O}_2})$$

The oxygen concentration affects the characteristic reaction time through both the concentration and temperature. Extinction data are obtained by fixing the oxygen flow rate and increasing nitrogen flow rate until blowoff results. Since the PVC curve in Figure 3 lies above the PE curve, PVC is the more inhibited (less reactive, more easily extinguished case), which is expected since no chlorine is in the PE flame.



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Figure 3. Extinction curves and adiabatic flame temperatures for PVC and PE with N_2/O_2 mixtures.

The scatter in the PVC data is due to the instability of the PVC flame near extinction. The commercial PVC produced an ash that had to be periodically removed. Sometimes knocking off the ash would extinguish the flame. The geometry of the PE surface changes as the nozzle velocity is increased. At low velocities a flat surface is obtained while at higher velocities a more rounded surface results. One expects that a rounded surface increases the burning rate in comparison to a flat surface.

RESULTS

The most important comparison, that of adding equal amounts of chlorine to both sides of the diffusion flame, is in Figure 4. The main point to note is that HCl is acting primarily as an inert. The position of the extinction curve for PE plus HCl has not changed much from the PE without HCl case. The extinction conditions were obtained by holding the HCl and O_2 flow rates constant, and increasing the N_2 flow rate to blowout.

That the HCl is acting as an inert can be further seen in Figure 5. The points for $\eta_{HCl}/\eta_{O_2} = 1/3$ correspond to the oxygen mole fraction at extinction for PE given in Figure 4. The curve for $\eta_{HCl}/\eta_{O_2} = 0$ indicates the change in the adiabatic flame temperature (for an equivalence ratio of one) if the HCl is replaced by N_2 . Accordingly, the adiabatic flame temperature is almost unaffected by whether HCl is added or the inert N_2 is added.

As a first guess one might have expected the amount of inhibition to be roughly the same for the two cases, since the same amount of chlorine inhibitor was added to both sides of the flame. The same amount of inhibition did not result. The HCl bond may be too strong,

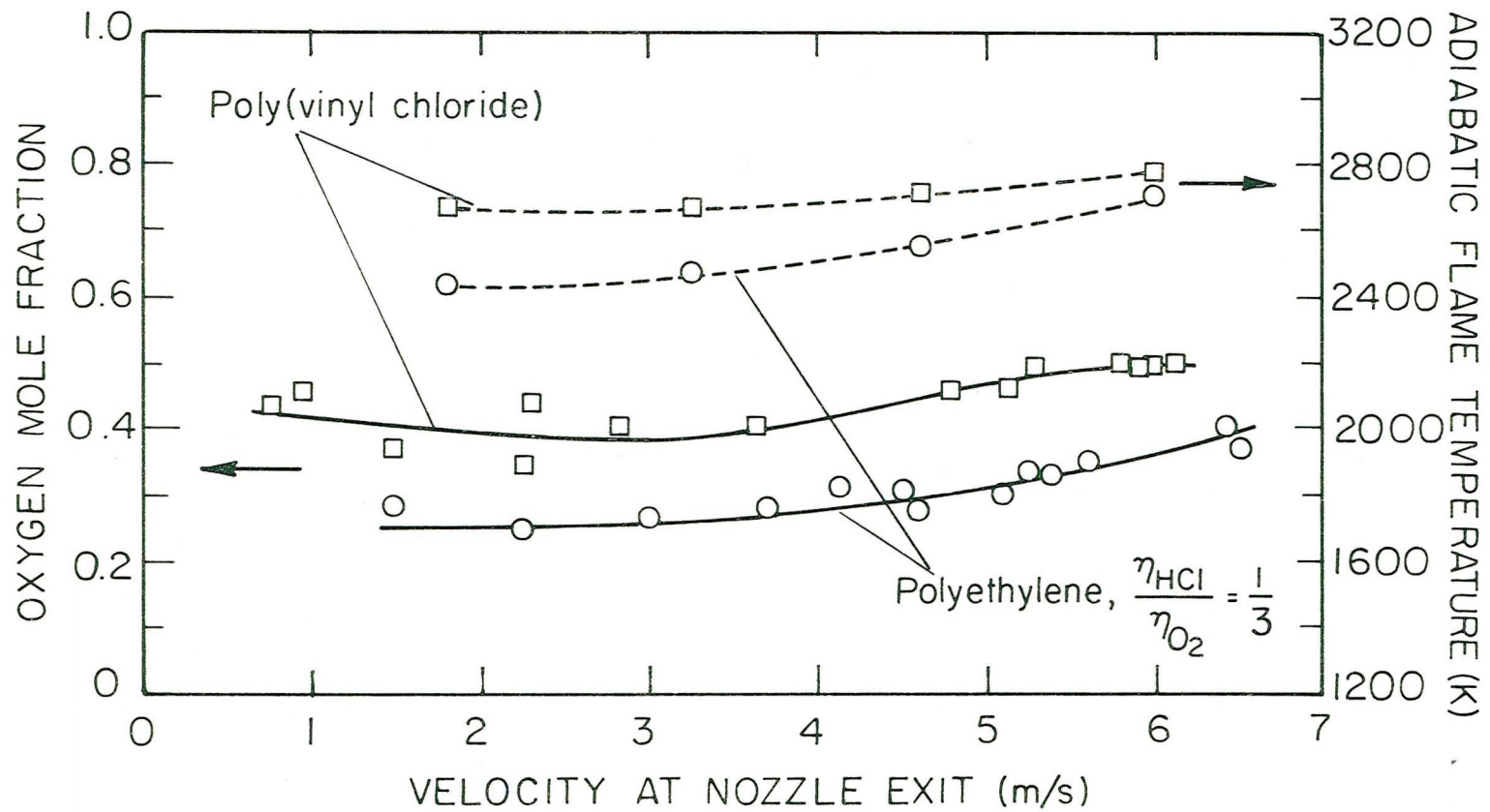
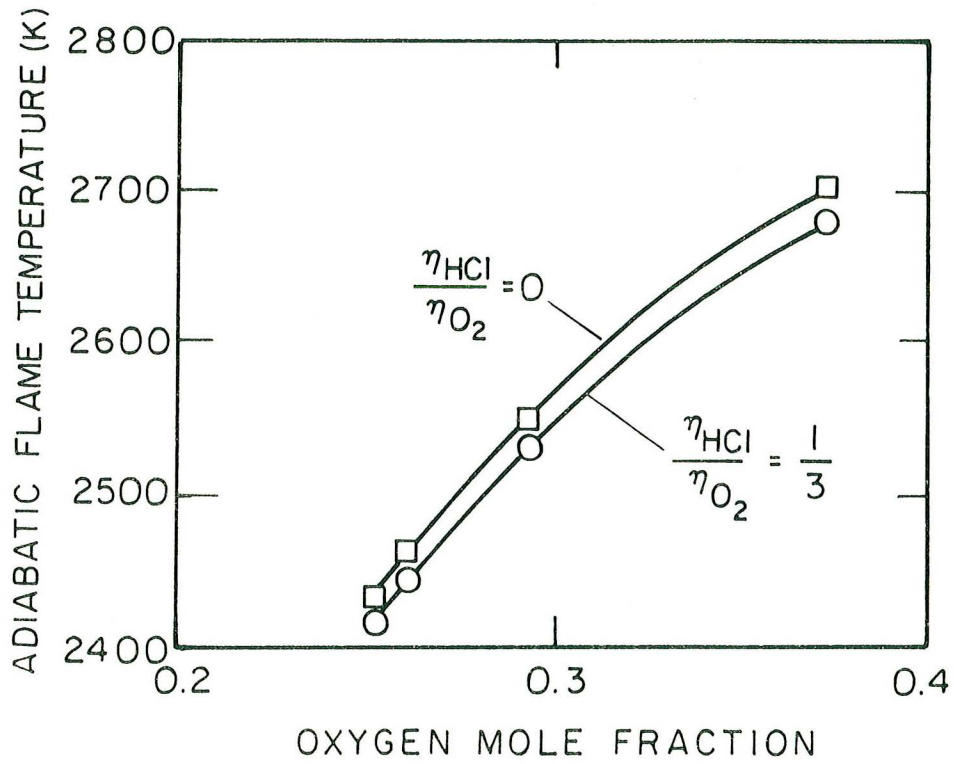


Figure 4. Comparison of extinction curves and adiabatic flame temperatures of PVC with N_2/O_2 mixtures and PE with $N_2/O_2/HCl$ mixtures where $\eta_{HCl}/\eta_{O_2} = 1/3$.

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Figure 5. Thermal effect on adiabatic flame temperature of adding HCl or nitrogen to polyethylene.

so that HCl does not interact with the flame chemistry. Additionally, PVC has a lower enthalpy of formation than PE (Table 1). Ignoring the effect of HCl, more energy is required to depolymerize PVC than PE. Also, the C-Cl bond in PVC is stronger than the C-H bond in PE. Consequently, more energy is required for total pyrolysis of PVC, which may contribute to a higher PVC extinction curve. The PVC extinction curve could also be influenced by previously discussed impurities in the commercial PVC. One impurity is commonly antimony which is a fire retardant itself. The impurities in the PVC may be instrumental in its ash formation. Ash increases surface radiation losses from the combustion system and may contribute to a higher PVC extinction curve.

The adiabatic flame temperature of PVC (all flame temperature calculations performed at an equivalence ratio of one) is higher than that of PE plus HCl at extinction conditions, Figure 4. This may reveal that the inhibitor chlorine is tending to increase the flame temperature yet lower the reaction rate chemically (Brown and Schefer, 1978). The net result is an extinction curve that lies at higher oxygen mole fractions for PVC than for PE with HCl added to the oxidizer. It should be noted that while the adiabatic flame temperatures are fundamental thermodynamic properties and give a limiting theoretical comparison point, there is no guarantee that they reflect the actual flame zone temperatures either in an absolute or in a relative sense. The actual flame zone temperature, especially near extinction conditions, would be anticipated to be affected by radiation heat loss, failure of the reaction to go to completion, and a local mixture ratio possibly different from stoichiometric.

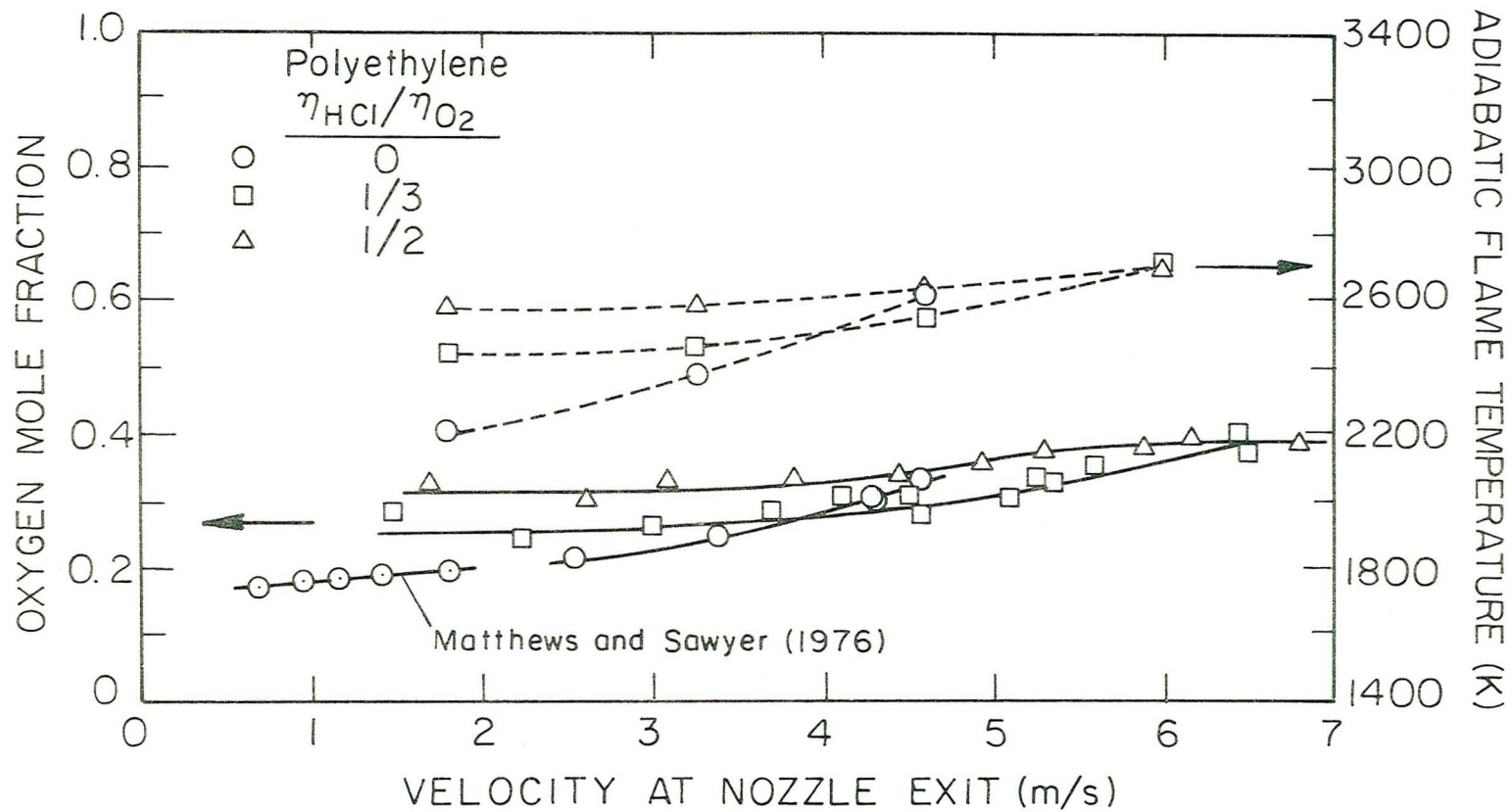
Further, the reactions important to chemical inhibition may be occurring in a region in the flame removed from the point of maximum temperature (Fristrom and Sawyer, 1971).

FURTHER HCl ADDITION

Another interesting question is the change in HCl effectiveness with HCl concentration. The result is shown in Figure 6. The extinction curves do shift slightly upward for higher $\eta_{\text{HCl}}/\eta_{\text{O}_2}$ ratios, implying an increase in inhibitor effectiveness. The HCl curves do not qualitatively lie in the same region as the PVC extinction curve. Again, the HCl seems to be behaving largely as an inert compared to Cl in PVC. However, since the higher concentrations of HCl do extinguish at higher oxygen concentrations and temperature, some chemical effect is apparent.

CONCLUSIONS

The behavior of the HCl added to the oxidizer side of the diffusion flame was primarily like an inert, although some chemical effect is apparent. This is in comparison to Cl being introduced in the fuel side by the PVC. Impurities in this commercial PVC may have an effect on the extinction curve. To determine the influence of impurities, extinction curves for reagent grade PVC will be found.



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Figure 6. Effect on extinction curves and adiabatic flame temperature of further HCl addition.

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