A Novel Method for Evaluating the Effectiveness of Low Volatility Flame Inhibitors with an Opposed-Jet Burner

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Introduction

In accordance with the Montreal Protocol, the US government has recently banned the manufacture of CF_3Br, a prevalent flame-inhibiting agent, due to its deleterious effect on the ozone layer. Consequently, there is great interest in finding chemically-active, flame-inhibiting alternatives [1]. Some attractive flame-inhibiting compounds, such as several phosphorus-containing compounds (PCCs) [2,3], are liquid at ambient conditions and have low vapor pressures. This paper presents a novel method to evaluate the effectiveness of such compounds.

The non-premixed counterflow configuration is useful for studying flame-inhibiting agents [4-6] because the flame is thermally isolated and two dimensional [7-9]. The flame strength can be characterized by the strain rate at extinction, which is well defined in this geometry and equal to the axial velocity gradient, measured just upstream of the flame along the centerline of the flow [7,9]. During an typical extinction measurement, both reactant flow rates are slowly increased until the flame abruptly extinguishes. For flame-inhibiting compounds that are low vapor-pressure liquids at room temperature, there are practical difficulties in establishing and maintaining constant loadings of the inhibitor as flow rates are adjusted. A novel method for performing extinction measurements is presented herein which provides a practical method for achieving constant inhibitor loadings.

A brief description of the apparatus and the results of an experimental evaluation of the novel method for methane/air flames are presented.

Experimental

Experiments were conducted on an opposed-jet burner. Methane diluted with nitrogen was used as the fuel and a mixture of oxygen and nitrogen as the oxidizer. By varying the methane and oxygen concentrations, a non-premixed flame can be stabilized on either the oxidizer or fuel side of the stagnation plane. The burner was aligned vertically with the lower tube used as the fuel source and the upper tube as the oxidizer source. A few experiments, conducted with the reverse orientation to study the effect of buoyancy, found no significant change in extinction strain rate. The burner was constructed from glass tubes 30 cm long with an ID of 0.98 cm, and a separation distance of 0.95 cm between opposing nozzles. Annular sheath flows of nitrogen are provided through 2.22 cm ID glass tubes. The sheath tube exits were offset by approximately 1 cm, upstream of the reactant tube exits, to minimize the impact of the sheath flow on the development of the reactant flows. The entire burner is isolated in a glass enclosure for control of exhaust gases. This enclosure is purged with nitrogen and maintained slightly below atmospheric pressure.

The T-shaped enclosure has a glass window on one end, approximately 25cm from the centerline of the flame. A video camera was located a few centimeters from this window, perpendicular to the radial flame direction, and used to measure flame position. Measurements of flame position were made on a television screen via a video camera with the flame as close to extinction as possible. Flame position was measured relative to the oxidizer nozzle exit plane and several cases were observed where the flame actually entered the nozzle. In this situation, the flame position was recorded as 0 mm. This measurement of flame position is used in verifying our novel method will be described below.

The flame inhibitor used during this investigation, dimethyl methylphosphonate (DMMP) $[P(=O)(CH_3)(OCH_3)_2]$, is a liquid at room temperature with a low vapor pressure (less than one torr at ambient temperature). In order to maintain sufficient concentrations of DMMP in the vapor phase, the reactant lines were heated to approximately 100°C with electrical heating tapes. The temperature of the reactant streams 10 cm upstream from the exit of the nozzles was maintained at 100±1°C via active control of the sheath flow temperature.

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The Novel Method for Conducting Extinction Measurements

One practical method of delivering small, metered quantities of low vapor pressure dopants, such as DMMP, to the reactant stream is via a syringe pump which provides a constant mass flow of the compound. Previous extinction studies using opposed-jet burners have adjusted the strain rate by varying both the oxidizer and fuel streams simultaneously so that the flame position remains constant [5], or so that a momentum balance between the two streams is maintained [4]. These methods of approaching extinction would result in variable concentrations of the inhibiting agent, due to the changing mass flow of the doped reactant stream and the resulting transients in the adsorption/desorption of the agent on walls. During our experiments, the concentration of DMMP in the reactant stream was fixed by maintaining a constant flow for sufficient time for the system to reach equilibrium. Then extinction conditions were approached by varying only the undoped reactant flow while maintaining a constant flow on the doped side. One of the consequences of using this method for approaching extinction is that the flame position varies during the extinction experiment. An investigation was conducted to determine the effect of flame position on the measured extinction strain rate.

This investigation was performed for two different stoichiometric mixture fractions, Zst, which can be evaluated from reactant compositions in the nozzles and the stoichiometry of the overall combustion reaction, using equation 1:

$$\text{Zst} = Y_{O,-\infty} \Big/ \left(\left(\frac{MW_O \nu_O}{MW_F \nu_F} \right) Y_{F,+\infty} + Y_{O,-\infty} \right), \tag{1}$$

where Y is mass fraction, MW is molecular weight, ν is the stoichiometric coefficient for complete combustion, the subscripts O and F refer to oxygen and fuel respectively, and the subscripts $\pm\infty$ refers to conditions at the fuel and oxidizer nozzles. An undiluted methane/air flame has a Zst = 0.054 and lies on the oxidizer side of the stagnation plane. As one increases Zst, the flame moves closer to the stagnation plane, until Zst = 0.5, where it lies on or near the plane itself. For Zst > 0.5, the flame will lie on the fuel side. The experiments presented herein were for Zst = 0.054 and Zst = 0.5.

Results and Discussion

There are two common techniques for determining the extinction strain rate in flame measurements: direct measurement of the local strain rate using procedures such as Laser Doppler Velocimetry (LDV), or estimation of the strain from global parameters. For our experiments, the extinction strain rate was estimated using the latter technique and will be referred to as the global strain rate, a_q. We use the following relation, proposed by Seshadri and Williams [10] based on a plug flow model, for evaluating the global strain rate:

$$a_q = \frac{2V_O}{L}\left(1 + \frac{V_F\sqrt{\rho_F}}{V_O\sqrt{\rho_O}}\right), \tag{2}$$

where L refers to the separation distance between the nozzles, V is the stream velocity and ρ is the stream density. Equation 2 is for the strain rate at the stagnation plane of a non-reactive flow. This global strain rate is used as an approximation to the local strain on the air side of the flame surface for flames near extinction. Modified expressions for strain have been developed to include, for example, flame thickness [11]; however, equation 2 has the merit of simplicity. Recent measurements [12] have revealed a proportionality between the global strain given by equation 2 and the local strain measured by LDV. Although the constant of proportionality is presumably dependent upon burner design, this proportional relationship makes this global strain formulation useful for determining inhibitor effectiveness.

Experiments were performed over a large range of fuel and oxidizer flows, achieving extinction with the flame in a variety of positions. Figure 1 shows results from experiments with Zst = 0.054. These results indicate that the global extinction strain rate remains fairly constant over a large range of flame positions, varying less than ±2% from a mean value of 359 1/s in the observed region from >0 to 7mm. This region will be referred to as the *acceptable* region. For experiments in which extinction occurs with the flame outside the acceptable region, large deviations in a_q occur. We attribute these deviations to effects of the nozzles on the flame and stagnation region. Further investigation of this effect and the obvious asymmetry of the acceptable region was performed with Zst = 0.5.

When Zst = 0.054, the flame exists on the oxidizer side of the stagnation plane which introduces an inherent asymmetry of the effect of the nozzles on the flame. Thus, if the flame is on the stagnation plane (i.e. Zst ≈ 0.5), this asymmetry is eliminated. The results of the Zst = 0.5 study are shown in Figure 2. Although there is greater scatter in the data, which we attribute to lack of repeatability in oxygen concentration, the global extinction strain rate varies less than 3% of the mean value of 336 1/s. The acceptable region for Zst = 0.5 does not appear to have the asymmetry observed for Zst = 0.054. This supports the hypothesis that as the flame and stagnation plane approach the nozzles, the flow field is affected.

The plateau of the acceptable region of Figure 1 slowly falls off starting around a flame location of 7mm. Other researchers have found, for a Zst = 0.054, the flame lies approximately 2mm above the stagnation plane [13]. This would agree with our results that at a flame location of 7mm, the stagnation plane is quite near the fuel nozzle.

As discussed earlier, for the typical case of Zst = 0.054, if extinction occurs in the acceptable region, the magnitude of a_q is consistent to within 2% of the result that would be obtained by maintaining a fixed flame position. A limited number of experiments with DMMP-doped flames confirmed that the region in which a_q was invariant with flame position was the same as that for the undoped case. The existence of this acceptable region establishes the validity of our method for approaching extinction with a constant oxidizer flux and dopant concentration, provided that the flame position at extinction lies within this region.

This novel method of approaching extinction does not necessarily require the cumbersome task of observing flame location at extinction for all measurements. Rather, a parameter S is introduced which can be calculated from the reactant stream properties at the nozzles. S approximates the distance from the oxidizer nozzle to the stagnation plane and is given by the analytical expression in equation 3, again derived by Seshadri and Williams from the plug flow model [10]:

$$S = L \Big/ \left(1 + \frac{V_F \sqrt{\rho_F}}{V_O \sqrt{\rho_O}}\right). \qquad (3)$$

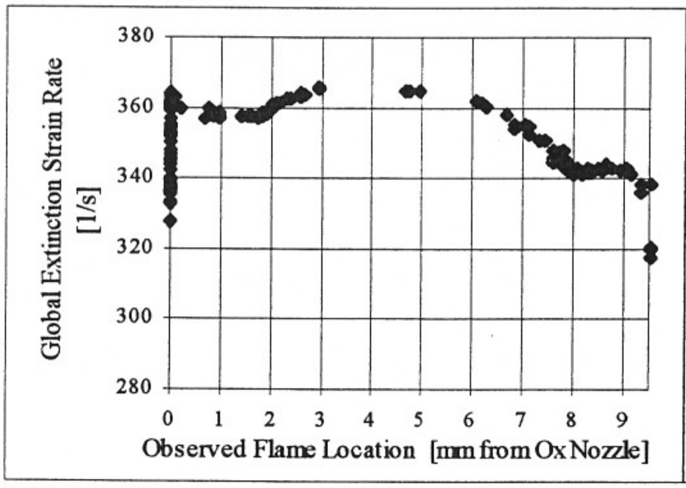

Figure 1. Acceptable Region, for Zst = 0.054. Global extinction strain approximately constant for Observed Flame Location between 0 and 7 mm.

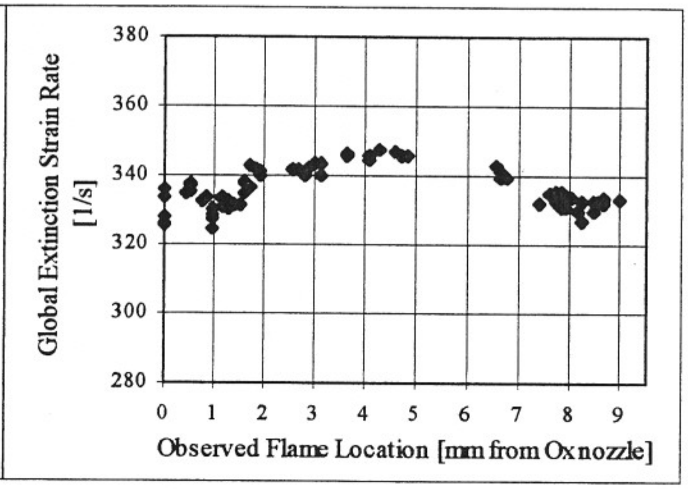

Figure 2. Acceptable Region, for Zst = 0.5.

Figure 3 shows a plot of observed flame location for both Zst = 0.5 and Zst = 0.054 against the parameter S. By noting that the observed flame location, for both conditions, is a well correlated one-to-one function of the parameter S, one can map the acceptable region in terms of S. For Zst = 0.0544, this region is 3.50mm < S < 5.25mm. Since S can be evaluated from known flow rates, direct observation of the flame becomes unnecessary.

Summary

A novel method for measuring the effectiveness of low vapor pressure phase flame inhibitors with an opposed-jet burner has been described. This method allows for a constant loading of the dopant by maintaining a constant flow in the doped reactant stream, but the flame moves as extinction is approached. It has been shown that the extinction strain rate remains constant to within 2% for a methane/air flame for a measured range of flame positions at extinction. The flame positions are a one-to-one function of an easily calculated quantity, S: the distance from the oxidizer nozzle to the stagnation plane.

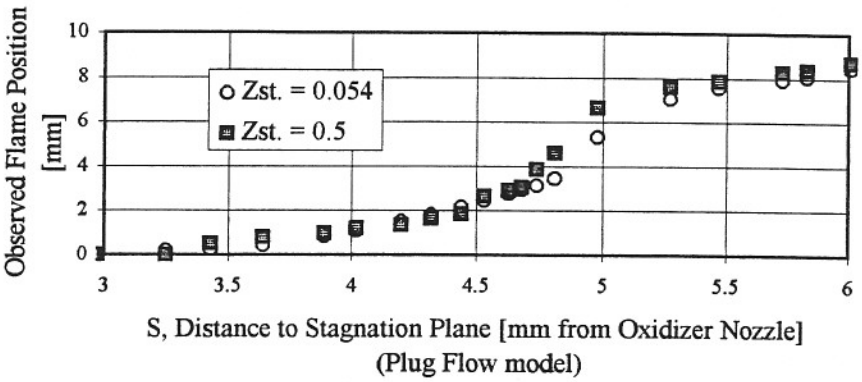

Figure 3. Variation of Observed Flame Position with the parameter S.

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