Parametric Study of Hydrogen Fluoride Formation in Suppressed Fires

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Abstract

Some of the proposed replacements for CF_3Br, the fluorinated hydrocarbons, are required in higher concentrations to extinguish fires and contain more halogen atoms per molecule. Since they decompose in the flame, they produce correspondingly more hydrogen fluoride than CF_3Br when suppressing a fire. Recent laboratory experiments with burners using heptane, propane, and methane have indicated that the amount of HF formed in steady state can be estimated within about a factor of two for diffusion flames and within 10% for premixed flames based on equilibrium thermodynamics. In this model for HF formation, the inhibitor molecule is transported to the reaction zone by convection and diffusion and is consumed in the flame sheet to form the most stable products (usually HF, CO_2, and COF_2). In the present work, the equilibrium model is used to estimate the upper limit of HF formation in suppressed fires. The effects of fuel and agent type, fuel consumption rate, and agent injection rate are included in the model, as are room volume, humidity, and concentration of inhibitor necessary to extinguish the fire. Results are presented for a range of these parameters, and the predictions are compared, when possible, with the results of laboratory and intermediate-scale experiments.

Introduction and Background

The chemical agent CF_3Br is an effective [1] and widely used fire suppressant. The current ban on its production, however, has lead to a search for alternative chemicals [2]. While no agent with all of the desirable properties of CF_3Br has been clearly identified, a number of alternatives have been proposed, and research is underway to evaluate their effectiveness [3]. The quantity of agent required to suppress various types of fires has been used as a measure of an agent's **utility.** In addition, the amount of any unwanted decomposition by-products formed during fire suppression has been identified as a potentially important parameter. The acid gases hydrogen fluoride, hydrogen chloride, and hydrogen bromide (HX, where X denotes a halogen), are thought to be the most damaging and dangerous of the potential decomposition products, and

much study has been devoted to determining the amounts of these chemicals formed during fire suppression by CF_3Br and halon alternatives [4-16]. While CF_3Br is known to readily decompose to form HF, HBr, and COF_2 in laboratory premixed and diffusion flames and in larger scale fires [17-23], the amounts were not considered to be a major threat compared to that of the fire itself. The alternative agents have been found to produce significantly more acid gas than CF_3Br, and consequently, there exists a need to understand and predict the mechanisms of formation of acid gases in laboratory flames, and ultimately, suppressed fires.

The quantities of acid gases formed in a large-scale suppressed fire will depend upon the properties of the fire itself, characteristics of the agent delivery system, and fate of the acid gases after their formation. The fire is essentially the source term for acid gas formation, since high temperatures are required for rapid agent decomposition'. The amount of HF formed will depend upon the fire size, fuel type, and flame type (premixed or diffusion). In addition, ease of extinguishment of the fire will be crucial, since for a given inhibitor, different fire types will extinguish at different concentrations for the same inhibitor. Flame extinguishment ease will be affected by the stabilization mechanisms, the flow field, and sources of re-ignition. The characteristics of the agent delivery system which will affect the quantity of HF formed include the agent type and the concentration at which it extinguishes the flame. The rate of introduction of the agent is important, as are the **mixing** rates in the protected volume and the delivery rate to the stabilization region of the flame. Finally, after formation of HF by the fire, the dispersion of the acid gas throughout the protected space will affect its peak and average concentrations. The space volume as compared to the fire size, the ventilation rate, and the presence of surfaces for acid gas condensation will influence the HF concentrations, which will vary both spatially and temporally. The rate of air **mixing** in the protected space may have a large effect on the final measured HF concentrations. Both the characteristics of the agent delivery to the fire and the fate of the HF after fire suppression--while greatly affecting the quantities of HF formed, may vary widely for different applications. Because this potentially wide variation, they are difficult to specify. The approach taken in the present work is to examine the source term, HF production in the fire, for a range of conditions. Specifically, the effects of fuel type, fire type and size, agent chemical composition and application rate, and room humidity are considered with respect to their effect on the HF formation, both for steady-state and transient conditions. The rates of HF generation can then be used as a source term in more detailed models which include the effects of variable mixing rates of the inhibitor, mixing rates of post-fire gases, ventilation rates of the space, and HF condensation to surfaces.

A model of HF formation has been developed based on equilibrium thermodynamics and diffusive transport in a simple physical model of the flame [24]. The model has recently been expanded to allow inclusion of the effects of water vapor in the ambient air. Previously, it has been tested against laboratory scale HF data obtained from a cup burner operating with propane or heptane, a laminar and turbulent jet burner operating with propane, and a premixed methane-air flame, all in the steady-state mode. Several transient experiments have now been conducted. The present paper describes the model and then summarizes some previously reported steady-state data. New data on HF formation in transient, suppressed flames are presented, and the theoretical model is used to predict the HF formed in these experiments. The HF concentration predicted by

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[1] for brevity, in the present paper, the formation of HF, HCl, HBr, and COF_2 will generally be described as "HF formation", except where specifically discussed.

the model are then compared with intermediate-scale results from the literature [25]. Finally, the model is used to illustrate the influence of some of the important parameters on HF formation.

Experiment

The experiment consists of a cup burner apparatus modeled after that of Booth *et al.* [26] and Bajpai [27], modified to operate on propane fuel as illustrated in Fig. 1, and described in detail elsewhere [28]. Measurements are made in both the steady-state mode and during transient suppression of the flame. In the steady-state experiments, the agent is added to the air stream at a concentration less than that necessary to extinguish the flame (nominally, 50 and 90% of the extinction concentration). A quartz probe extracts a measured fraction, approximately 0.5%, of the total flow of hot product gases for a period of sixty seconds, and a water bubbler traps the HF and COF_2. After the sample is collected, ion-selective electrodes determine the F concentration in the bubbler. The air, fuel, and inhibitor gases supplied to the burner are metered with calibrated mass flow controllers, while the flow of sample gases are measured with a calibrated rotameter located downstream of a cold trap or desiccant dryers. In the transient experiments, the agent is added to the air flow at a concentration increasing linearly in time up to a value 25% above the cup burner extinction concentration. The concentration ramp, implemented through computer control of the mass flow controllers, allows effective ramp times from 5 seconds to any number of minutes. Because the amount of HF formed is lower than in the steady-state experiments, a higher sample gas flow is used (about 7% of the total flow), and a second bubbler insures that no HF is untrapped. In the experimental procedure, the gas sample flow is started, the inhibitor is ramped up in concentration to 125% of the flame extinguishment concentration and the flame extinguishes. The sample flow continues 30 seconds after extinguishment and is stopped. The sample probe consequently extracts a measured fraction of the total product gas flow, from which the total HF formed is determined.

Model for Acid Gas Formation

A model for acid gas formation has been developed based on a simple Burke-Schumann model [29] of a co-flowing jet diffusion flame with fuel in the center and air co-axial. In the Burke-Schumann analysis, the fuel is assumed to be consumed at a reaction sheet, where fuel and oxidizer come together in stoichiometric proportions and the temperature reaches its highest value (which can be approximated by the adiabatic flame temperature of a stoichiometric premixed flame). The height of the flame is determined by the jet diameter and the rate at which the oxidizer can diffuse to the center-line of the fuel jet. The present flames differ in that the air stream contains inhibitor in addition to oxidizer.

In the present analysis, the inhibitor is assumed to be consumed in the reaction zone as a reactive species. This assumption is based on premixed flame measurements and modeling [30-34.]. For both brominated and fluorinated carbon compounds, complete consumption of the inhibitor is typical. In many cases, the inhibitor is consumed faster than the fuel itself. Extensive thermodynamic equilibrium calculations of the composition of fuel-air mixtures in the presence of halogenated inhibitors also indicate complete exothermic conversion of the inhibitors to HF, CO_2

COF_2 and water. The agent can be thought of as an additional fuel species, having its own oxygen demand, yet coming from the air side of the flame. It must diffuse to the hot reaction zone which serves as a sink for the inhibitor. Thus fuel, oxygen and inhibitor are consumed in the reaction zone in stoichiometric proportions, with the stoichiometry determined from a balanced chemical reaction to the most stable products. Transport rates of inhibitor and oxygen are based on their relative rates of diffusion [28] incorporating molecular weight effects. *An* implicit assumption in the present analysis is that the characteristic height for reaction of the fuel with oxygen is the same as the characteristic height for decomposition and reaction of the inhibitor. Given the inhibitors' preference for reactions with hydrogen atom [35] and the high concentration of these species near the flame sheet, this assumption is reasonable. Presently, it is also assumed that there is always sufficient air for complete combustion of the inhibitor and fuel. Hence, the estimate of HF formation is an upper limit since fuel rich flames will extinguish more easily and consequently produce less HF.

Figure **2** illustrates some basic features of the model for a steady-state propane-air cup burner diffusion flame with C_3F_8 in the air stream. In this figure, the fluxes of hydrogen and fluorine atoms into the reaction zone are illustrated as a function of the C_3F_8 mole fraction in the air stream. At zero inhibitor mole fraction, all of the hydrogen input to the flame is converted to H_2O. As the inhibitor is added and fluorine becomes present in the reaction zone, hydrogen fluoride is formed preferentially over water (it is more stable). When all of the hydrogen has been consumed as HF, there is no water in the final products; any additional fluorine reaching the reaction zone shows up primarily as COF_2. The utility of this plot is that the HF production cannot be greater than the hydrogen or fluorine flux to the reaction zone; also, the sum of HF and COF_2 (the only significant other final species for fluorine) cannot be greater than the fluorine flux. For C_3F_8 in a propane-air flame, all of the hydrogen comes from the fuel, so that at zero inhibitor concentration there is a non-zero hydrogen flux to the reaction zone and additional inhibitor in the air stream does not increase the hydrogen flux to the reaction zone (for other inhibitors, such as C_2HF_5, increasing amounts of inhibitor slightly increase the hydrogen flux to the reaction zone). Conversely, all of the fluorine comes from the inhibitor, so it increases nearly linearly with the inhibitor mole fraction **Xi.** Since COF_2 readily hydrolyses in water to form fluoride ion F, measurements of fluoride typically include that from both HF and COF_2. In principle, the product gases from inhibited flames near extinction could contain the fluorine levels from both HF and COF_2. Interestingly, however, the experimental results for a number of fuels and agents [28] indicate that measured fluorine levels are rarely above the limit imposed by the hydrogen flux shown in Fig. 2. These reduced fluoride levels may be due to kinetic limitations on the rate of inhibitor consumption and HF formation [35].

The model developed can estimate the quantities of HF formed in flames when inhibitor is added to the air stream in steady-state at concentrations up to the extinction value. Selected experimental results for steady-state propane-air flames are presented in Figs. **2,** 3, **4,** and 5 for C_3F_8, C_3HF_7, C_2HF_5, and CF_3Br. Also shown are the estimated flux of hydrogen and fluorine into the reaction zone. These correspond to estimated upper limits on the HF formation: the fluorine limit is used for fluorine to hydrogen ratios F/H less than one, while the hydrogen limit is used for F/H **> 1.** The experimental results are typically within 30% of the prediction for the hydrogenated fluorocarbons, which is good considering the simplicity of the model. Perfluorinated agents produce HF at rates significantly less, up to 50%, than predicted based on equilibrium thermodynamics. These agents are believed to react more slowly in the flame. A

detailed understanding of the apparent chemical kinetic limitations to HF formation for the perfluorinated agents at all concentrations as well as for hydrofluorocarbons at high fluorine loading should be possible using a recently developed chemical kinetic mechanism for fluorine inhibition of hydrocarbon flames [36]. For the present analyses, however, the predicted acid gas formation in inhibited flames is based on equilibrium thermodynamics assuming that HF (not COF_2) is the source. Provision is also made in the model for inclusion of an empirical parameter, based on the experimental results, which describes the observed deviation from the equilibrium prediction in diffusion flames for which experiments have been performed.

The steady-state results are used to obtain results for transiently suppressed flames. In the present analyses, the inhibitor concentration in the air stream is assumed to increase linearly in time up to the extinction concentration for the particular flame (although any known profile of concentration versus time may be used). At each value of the inhibitor concentration, the production rate of HF is determined from the steady-state equilibrium model described above, providing a plot of the HF generation rate as a function of time. Integration of this curve provides the total HF formed during suppression of the flame. The inhibitor concentration as a function of time is provided as input, as is the concentration of inhibitor necessary to extinguish the flame. The stoichiometric model described above provides the HF production as a function of inhibitor concentration in the air stream per mass of fuel consumed, and the steady-state HF production at each concentration up to extinction is integrated to provide the total HF produced during suppression.

Comparison with Experiments

Experiments with propane-air diffusion flames (125 W) extinguished by C_2HF_5, C_3HF_7, and C_3F_8 were performed with variable injection rates of inhibitor so that the extinction time varied. The results are shown in Figs. 6,7, and 8 respectively, where the total mass of F produced during the extinction event is plotted as a function of the extinction time. *Also* indicated in the figures are the predicted HF formed using the stoichiometric model assuming equilibrium products (solid lines), and using the model in which the steady-state HF production rates are determined from empirically determined deviations from full equilibrium based on the steady-state results. *As* the figures show, in either case, the model is able to predict the results within the experimental scatter.

Extensive intermediate-scale tests of HF production by CF_3Br and halon alternatives have been reported by Sheinson *et al.* [25]. In order to further test the present model, we have attempted to predict the HF formed in their experiments. The experiments consisted of 0.23 and 1.1 m^2 heptane pool fires extinguished by CF_3Br, CF_3H, C_2HF_5, and C_4F_{10}. The agents were injected at varying rates and to different final inhibitor concentrations in the 56 m^3 protected space. The reported HF concentrations represent the peak measured values at a single fixed location. The results of their experiments (for the 0.23 m^2 pools) are shown in Fig. 9, which provides the measured HF mole fraction (in ppmv) as a function of the fire out time for the four agents. Although the experimental data represent different agent injection rates and final design concentrations of inhibitor, we have included all of the data in a single plot. The large scatter in the data probably occur from the effects of these additional parameters. Of these three parameters, injection rate, design concentration, fire-out time, we believe the latter to be most important in determining the HF production and have made it the independent parameter. The

results of the stoichiometric model based on achievement of full equilibrium are given by the solid line. In these calculations, the model predicts the total mass of HF produced. In order to allow a comparison, it is necessary to assume a spatial distribution of HF. Although there will be gradients of HF concentration in the room, we have assumed uniform distribution. As the figure shows, the predicted HF concentration agrees well with the experiments for each of the agents. Having gained confidence in the ability of the model to predict some experimental results, we now proceed to investigate the effect of several parameters on HF production in suppressed fires.

Parametric Analyses

The effect of various parameters on the production of HF can now be examined using the stoichiometric model. Figure 10 shows the calculated steady-state HF production rate (gm HF/gm fuel) as a function of the inhibitor mole fraction in the air stream for the inhibitors C_2HF_5, C_3HF_7, C_3F_8, and CF_3Br. The results are calculated for heptane, and the calculations are performed for dry air (solid lines) and for air with 2.3 mole percent water vapor (dotted lines), corresponding to 100 % R.H. at 25 C. Each curve is truncated at the extinction concentration in a heptane cup burner flame for that inhibitor. The area under each curve from zero inhibitor up to the extinction concentration represents the total HF formed for an extinguished flame (in gm HF/gm fuel consumed). If the fuel consumption rate is larger or the inhibitor injection rate is slower, the total fuel consumed during the extinction event is larger, and the HF formed is proportionally greater. The effect of water vapor is small when the agent concentration is low, but becomes important when there becomes more fluorine in the flame (the crossing point of the curves in Fig. 2 and the point of discontinuity in Fig. 10). The agent CF_3Br makes less HF because at a given mole fraction, the molecule carries fewer fluorine atoms into the flame than the larger halocarbons, and because it puts the flame out at a much lower concentration.

Figure 11 shows the quantity of HF produced by extinguished flames for three fuels, methane, propane, and heptane, CH_4, C_3H_8, and C_7H_{16}, and four agents, C_2HF_5, C_3HF_7, C_3F_8, and CF_3Br. The calculations assume dry air and the extinction values from cup burner flames. The quantity of HF produced is linear in both extinction time and fuel consumption rate. Fuels with higher H/C ratios (e.g. methane) may produce up to 50% more HF than fuels with lower H/C ratios such as heptane. The agents C_2HF_5, C_3HF_7, and C_3F_8 are expected to form quantities of HF that are within about 10% of each other, and about a factor of four more than will CF_3Br. Note that the deviations from equilibrium results experienced in the steady-state experiments can change the relative quantities of HF by up to a factor of two for an agent.

In the above figures, the extinction condition of the fire was assumed to be equal to the cup burner extinction value for the agent and fuel. If the flame is more easily extinguished, less acid gas will be produced during extinction. Because the curves in Fig. 11 are non-linear, the integrals of the curves are slightly non-linear as well. This is illustrated in Fig. 12 which shows the quantity of HF produced by heptane-air flames at 100% R.H. extinguished by C_2HF_5, C_3HF_7, C_3F_8, and CF_3Br as a function of the flame's extinction concentration for a constant extinction time (10 s). As the figure illustrates, flames which extinguish at lower concentrations of inhibitor produce less HF, in an approximately linear fashion. It should be emphasized that the analyses displayed in Figs. 10 to 12 examine the effects of several parameters on the HF source, the fire, under the assumption of thermodynamic equilibrium. As shown in Figs. 3,4, and 5, there can be

significantly less HF formed than predicted by chemical equilibrium. Further research is necessary to understand the chemical kinetic limitations to HF formation in inhibited diffusion flames.

Conclusions

The stoichiometric model, based on relatively simple but fundamental assumptions, is a useful tool for understanding HF formation in suppressed fires. The predictions of the model provide good estimates of the upper limit for formation of HF, and are valid for both steady-state and transient modes of inhibition. The predictive model indicates that HF formation will increase approximately linearly with fire size, extinguishing time, and the concentration at which the flame extinguishes. In addition, HF formation will be affected somewhat by the hydrogen to carbon ratio of the fuel, hydrogen to fluorine ratio in the agent, and the water vapor content of the air.

While predictions of HF produced in suppressed flames and intermediate scale fires are within about 25% of the experimental results (which have large scatter), the estimated quantities of HF formation based on chemical equilibrium can overestimate the steady-state HF production by up to a factor of two for some agents. **An** examination of the chemical kinetics of suppressed diffusion flames can lead to an understanding of the relevant phenomena, and may indicate approaches for reduction of the HF production by halon alternatives.

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Figure Captions

Figure 1 - Experimental apparatus for co-flow diffusion flame studies of acid gas formation in inhibited propane-air diffusion flames.

Figure **2** - Stoichiometric model prediction of hydrogen and fluorine flux into the reaction zone of a propane-air diffusion flame with varying amounts of C_3F_8 in the air stream. The fate of the hydrogen and fluorine are indicated for each regime of inhibitor concentration. Experimental results from diffusion flames [24] are indicated by the symbols.

Figures 3, 4, and 5 - Measured HF production rates in co-flow propane-air diffusion flames [24] inhibited by C_2HF_5, C_2HF_7 and CF_3Br. Data are shown **for** two diffusion flame burners at 50 and 90% of the extinction concentration for agent added to the air stream

Figure 6, 7, and **8** - Total fluoride produced (points) during suppression of a cup burner propane-air diffusion. The mass of **F** produced is shown **as** a function of the extinction time for the inhibitors C_2HF_5, C_3HF_7, and C_3F_8 ,respectively. The solid line presents the predicted amount of fluoride produced using the stoichiometric model with reaction to equilibrium products, while the dotted line represents the prediction corrected for the deviations from the equilibrium values of HF experienced in the steady-state experiments.

Figure **9** - Experimental data of Sheinson *et al.* **[25] for** intermediate-scale tests of HF production in extinguished heptane pool fires, together with predictions of stoichiometric model for suppression by CF_3Br, CF_3H, C_2HF_5, and C_4F_{10}. The data represent various values of injection rate and **final** inhibitor concentration. The model assumes chemical equilibrium. The open symbols terminating the lines identify the corresponding data.

Figure 10 - Stoichiometric model predictions of the HF formed in heptane-air flames **under** steady-state conditions with C_2HF_5, C_3HF_7, C_3F_8, and CF_3Br added to the air stream at various concentrations. The solid lines assume dry air and the dotted lines, a water mole fraction of **2.3%.**

Figure 11 - Total HF produced during extinguishment of a flame predicted by the stoichiometric model as a function of extinction time for three fuels, CH_4, C_3H_8, and C_7H_{16}, and four agents, C_2HF_5, C_3HF_7, C_3F_8, and CF_3Br. Dry air and cup burner extinction values are assumed.

Figure 12 - Total HF produced during heptane-air flame extinguishment as predicted by the stoichiometric model as a function of the extinction concentration **for** C_2HF_5, C_3HF_7, C_3F_8, and CF_3Br, assuming wet air and a 10 s extinction time.
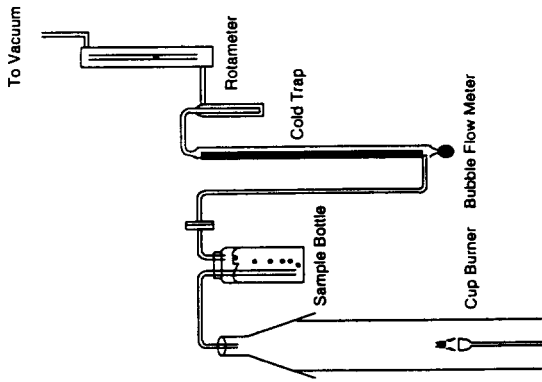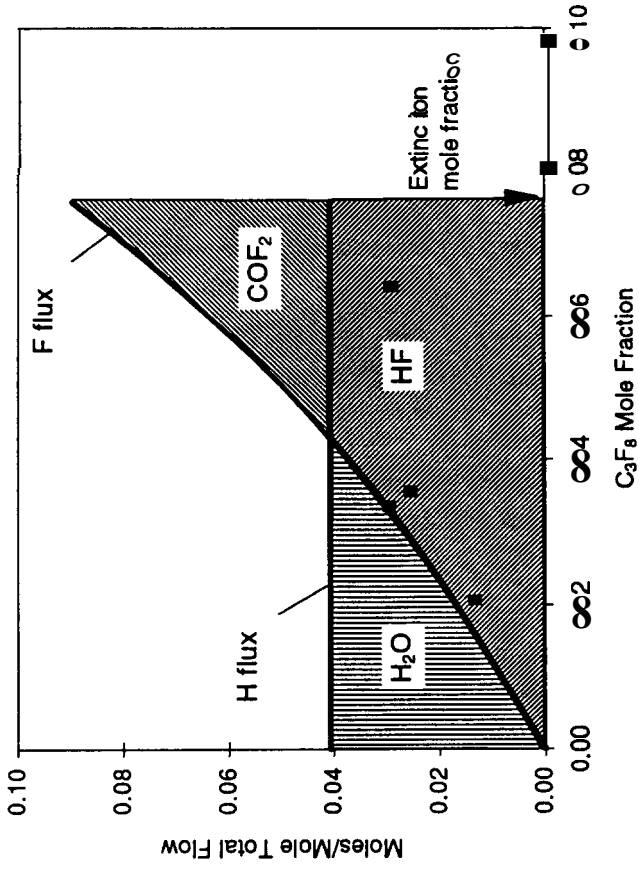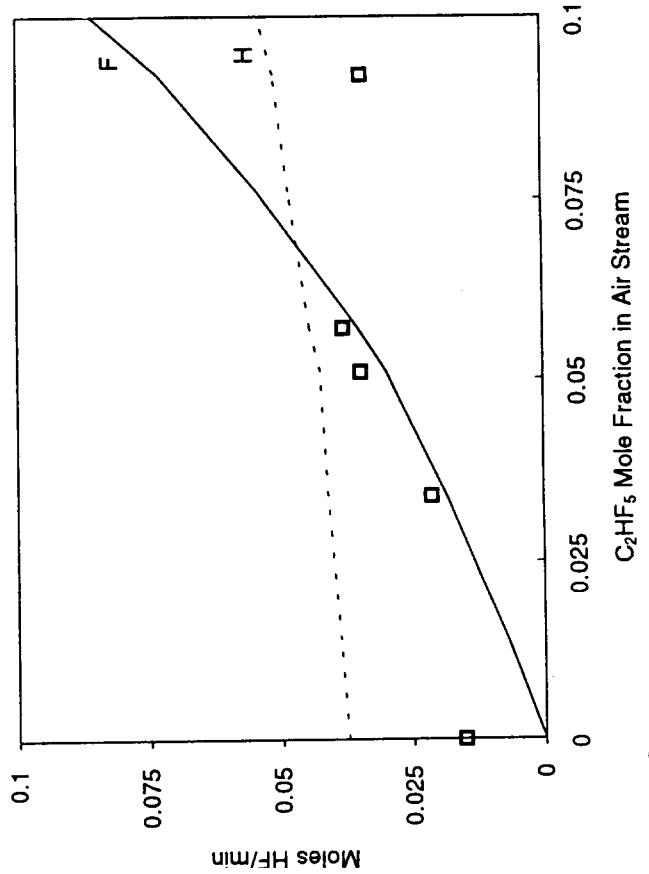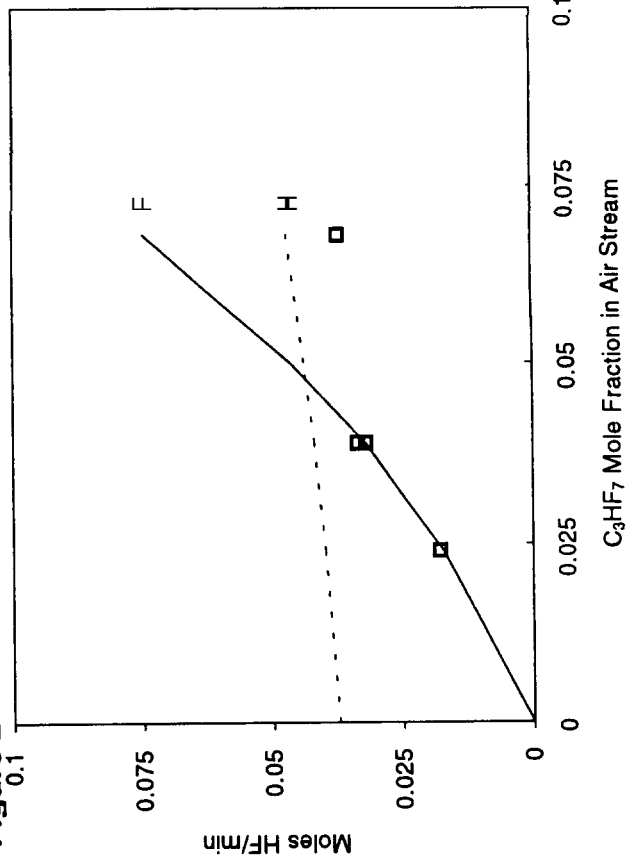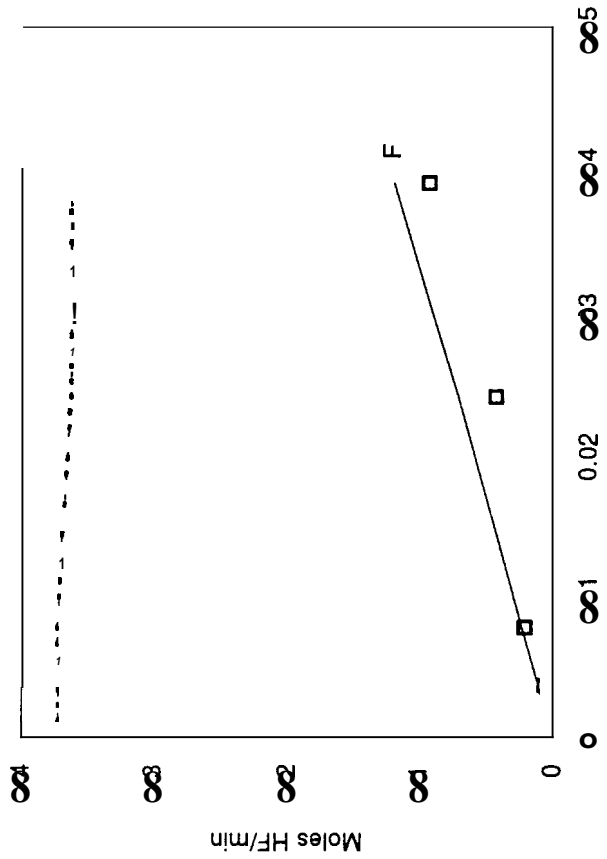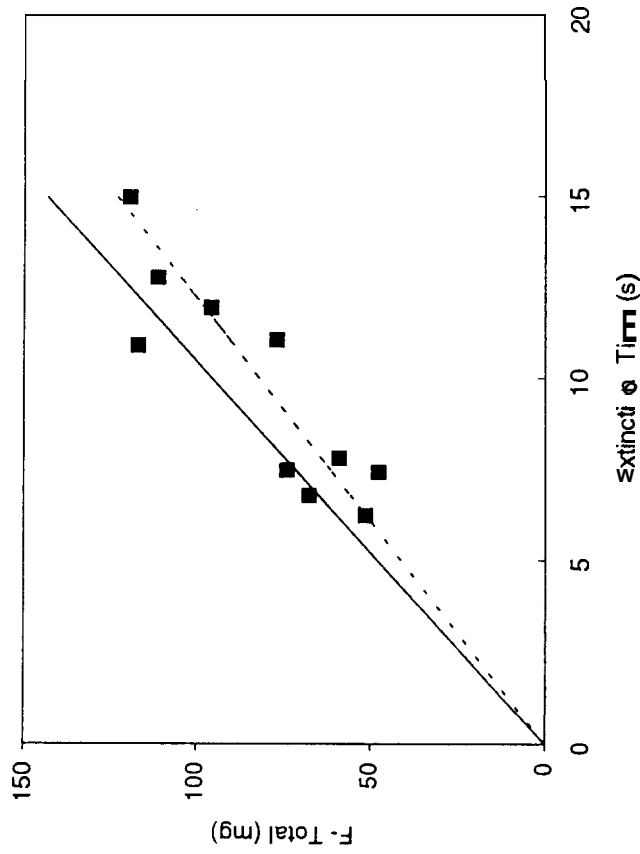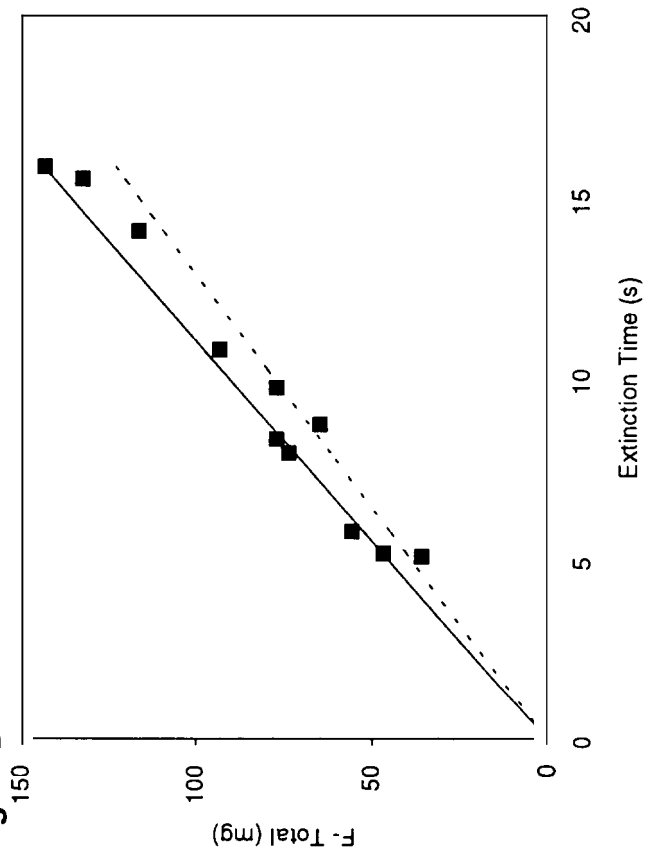
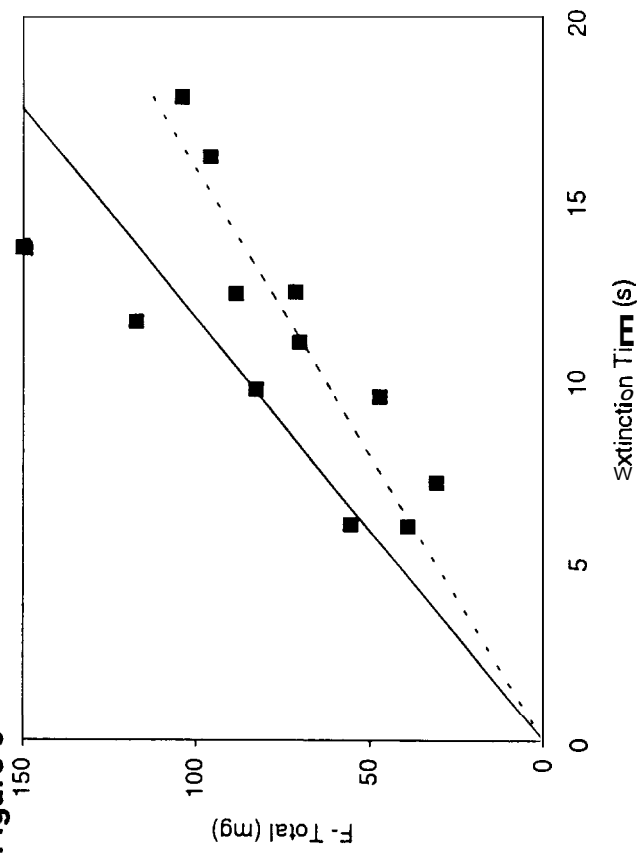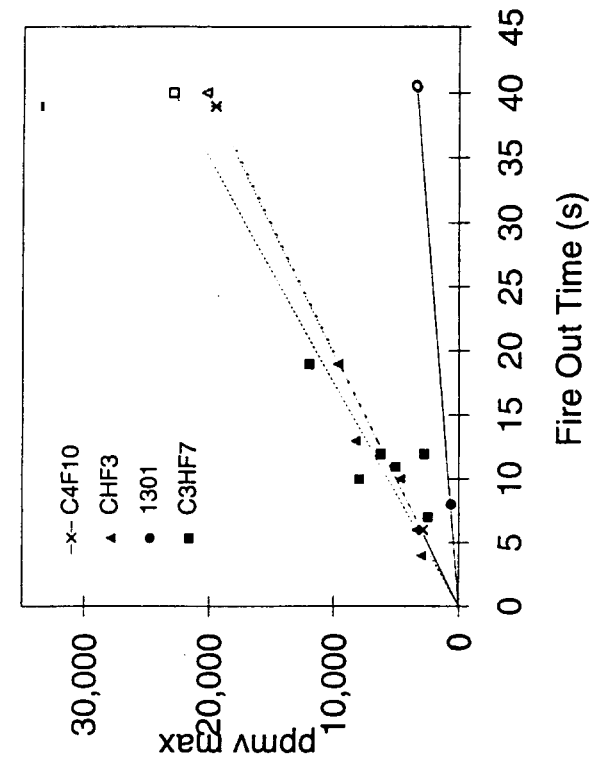Figure 2
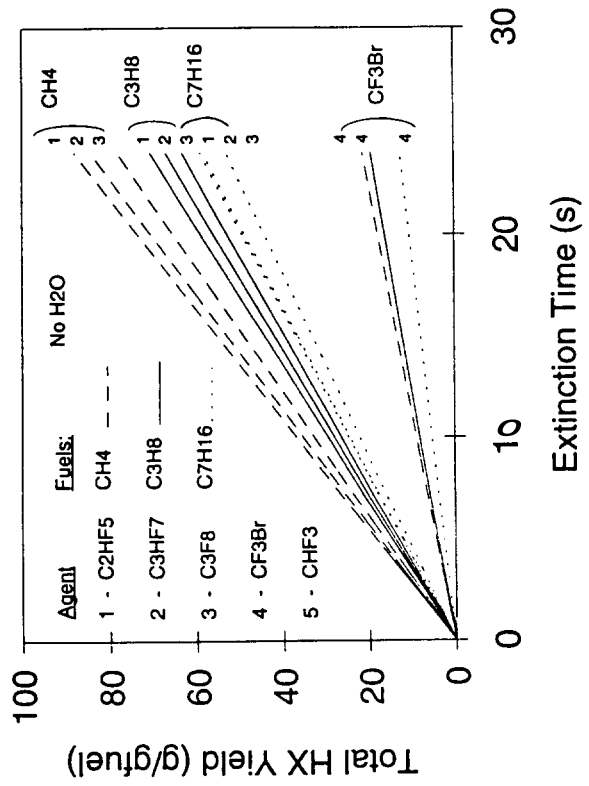

Figure 4

Figure 1

Figure 3

Figure 6

Figure 8

Figure 7

Figure 9

Figure 10

Figure 11

Figure 12