Production Mechanisms for Carbon Monoxide in Enclosure Fires

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1. INTRODUCTION

Roughly two thirds of all deaths resulting from enclosure fires can be attributed to the presence of carbon monoxide (CO) [1],[2] which is known to be the dominant toxicant in fire deaths [3]. The mechanisms responsible for the generation of high concentrations of CO in fires are poorly understood. A long-term program (Carbon Monoxide Production and Prediction Priority Project) at BFRL is seeking to develop an understanding of and predictive capability for the generation of CO in fires. [4]

Workers at Harvard University [5],[6],[7] and the California Institute of Technology [8],[9],[10],[11] have investigated the combustion products trapped in hoods located above fires burning in an open laboratory. These experiments were designed to be simple physical models for two-layer burning in enclosure fires. By varying the separation of the burner and the base of the upper layer and the fuel release rate, it was possible to control the amount of air entrained by the fire plume before entering the layer. The mass ratio of fuel and air entering the hood was given by the ratio of the flow rate of the fuel and the entrainment rate of air into the fire plume. Usually, such experiments were allowed to come to a steady state for which the upper-layer combustion gases had the same fuel-to-air mass ratio as the fire plume. The mass ratios in the upper layers were normalized by dividing by the mass ratio of fuel and air required for stoichiometric burning to yield the parameter known as the global equivalence ratio (GER, ϕ_g).

The hood experiments showed that concentrations of individual combustion species in the upper layer could be correlated in terms of the GER. The correlations were found to be independent of nominal heat release rate and burner/upper-layer separation. However, a dependence of combustion product concentrations on upper-layer temperature was identified. [9],[11] At lower upper-layer temperatures (less than approximately 850 K) oxygen and fuel molecules (e.g., original fuel, H_2, and CO) were observed to exist together for $\phi_g >$ 0.5. For higher temperatures and a lean upper layer, the fuel levels were reduced, while for rich conditions the oxygen concentration approached zero. The correlations were also shown to depend on fuel type. [5],[6],[7] Morehart et al. have reported an experiment in which air was introduced directly into the upper layer as well as entering through the fire plume. [9],[10],[11] In these cases the GER was reduced from the plume equivalence ratio. Remarkably, the same correlations of combustion gases with the GER were found as when the fire plume was the only source of gases in the upper layer. The existence of the correlations in the hood experiments has been termed the *Global Equivalence Ratio Concept.* Clearly, if the GER Concept could be applied to enclosure fires it would provide a powerful means for predicting the formation of CO.

Researchers at Virginia Polytechnic Institute and State University (VPISU) [12],[13] have investigated the formation of CO by fires within a model compartment. The facility at VPISU was especially designed to create an environment similar to that of the hood experiments. Air entered through long slots in the floor of the enclosure and combustion products were exhausted through a vent in one side. Such a configuration ensured a well defined, two-layer environment. The upper layer was shown to be uniform and well mixed. An equivalence ratio was obtained as the ratio of mass rates of fuel injection and air flow into the enclosure normalized by the stoichiometric ratio. The fires grew slowly so they were in a pseudo-steady state, and the measured equivalence ratios were roughly equal to ϕ_g. Concentrations of CO, CO_2, and O_2 were measured by extracting gases from the upper layer. The fuels studied were hexane, PMMA, wood, and polyurethane foam containing 45% by weight of inert filler.

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Measured concentrations of combustion gases in the upper layer of the enclosure were shown to correlate well in terms of the GER. The resulting correlations for hexane, wood, and PMMA were compared with those reported by Beyler [6],[7] for the same fuels in a hood experiment. The correlations agreed quite well for lean conditions. For rich conditions, the correlations were found to be qualitatively similar, but there were differences which were attributed to the temperature effect identified in the hood experiments. Differences between the two experiments were consistent with the higher upper-layer temperatures observed in the enclosure fires. Gottuck et al. concluded that the GER concept is valid for predicting CO formation for their enclosure once the temperature effect was accounted for. [12],[13]

The hood experiments and the VPISU enclosure study have shown that a mechanism for the generation of CO in enclosure fires is the quenching of a fire plume by a rich upper layer. The GER concept appears to offer an effective means for predicting CO when this is the dominant mechanism for CO production.

The VPISU experiments configuration is certainly more representative of enclosure fires than the hood experiments, but the use of separate pathways for air entering and combustion gases exiting the enclosure is not typical of the ventilation pathways in most enclosure fires. An experimental system has been developed at NIST which is a scale model of a standard full-scale enclosure used for fire testing. This manuscript reports measurements using this facility which show that two additional mechanisms for CO formation are possible in enclosure fires.

2. EXPERIMENTAL SYSTEM

A facility has been constructed at NIST for the investigation of CO formation in enclosure fires. [14] This system, dubbed the reduced-scale enclosure (RSE), was a 2/5-scale model of a full-scale room used in standard ASTM and ISO fire tests. The 0.98 m (width) x 1.46 m (length) x 0.98 m (height) enclosure has a 0.48 m x 0.81 m doorway. The RSE was located under a furniture calorimeter which collected the combustion gases exiting the doorway and allowed measurements of heat release rate as well as the relative concentrations of CO and CO_2 for positions far from the enclosure.

Conditions within the RSE were characterized by concentration and temperature measurements. Concentrations were obtained by extracting gases from two locations (generally in the front and rear of the upper layer) and using two banks of analyzers containing a paramagnetic analyzer for oxygen and non-dispersive infrared (NDIR) analyzers for CO and CO_2. Vertical arrays of thermocouples were used to record temperature profiles in the front and rear of the enclosure. For a few tests a total hydrocarbon analyzer was used to measure unburned fuel, and an instrument, dubbed the ϕ-meter, which was designed and built at NIST [15], recorded the local equivalence ratio for combustion gases extracted from the enclosure.

The fuel source for the fires was a 15 cm natural-gas burner placed at the center of the RSE. By varying the fuel flow rate it was possible to vary the nominal heat release rate (HRR) for the fires. A range of 25-650 kW was considered. Fires were burned long enough to achieve pseudo-steady-state burning.

A series of tests were also performed in which the ceiling and upper walls (34 cm band at top) were lined with 6.4 mm thick plywood. For these tests, the natural gas burner was also used and the same measurements were recorded as for the unlined tests.

3. EXPERIMENTAL RESULTS

The time behaviors of the concentrations of O_2, CO, CO_2, and H_2O in the front and rear of the enclosure are shown in Fig. 1 for a 500 kW fire. This fire is significantly underventilated. By averaging over the pseudo-steady state burning periods, concentrations typical of each fire HRR were obtained. Figures 2 and 3 show concentrations of CO and O_2 measured in the front and rear upper layers as a function of nominal HRR. The CO concentrations begin to increase for HRR > 200 kW, and the levels reach asymptotes which

are higher in the front ($\approx$ 2.8%) than in the rear ($\approx$ 1.8%). Unlike the hood experiments and enclosure studies of Gottuk et al. [12],[13], the upper layer is not well mixed. The nonuniformity of the upper layer is also reflected in the temperature measurements. For rich fires, temperatures in the upper layer near the front of the RSE approached 1300 K, while in the rear temperatures were generally hundreds of degrees cooler. Oxygen concentrations fall with increasing HRR rate and approach zero near the HRR of 200 kW where the CO concentration starts to increase.

Measurements using the ϕ-meter showed that a HRR of 200 kW roughly corresponds to a GER of 1. If it is assumed that GER values are proportional to HRR, this allows the observed concentrations to be given as a function of ϕ_g.

Figure 4 shows the concentrations of CO in the front and rear of the upper layer as a function of time during burning of a 600 kW natural-gas fire with the RSE lined with wood as described above. During the period when the wood was in the upper layer (the wood fell off the walls and ceiling at $\approx$ 650 s), extremely high levels of CO were detected in the rear of the RSE and the concentrations in the front were elevated $\approx$ 50% compared to a fire in which wood was not present. After the wood fell to the bottom of the enclosure, there was significant burning within the lower layer, but the concentration of CO dropped markedly in both the front and rear of the upper layer.

4. DISCUSSION

Toner [8] and Morehart [9] have reported concentration measurements for combustion species trapped in a hood above an open natural-gas fire. Since the upper-layer temperatures were higher for the Toner experiments, concentrations of major species found in the RSE, where upper-layer temperatures were much higher than observed in the hood experiments, were compared with his results. Results for CO, CO_2, and O_2 within in the upper layer in the rear of the RSE were found to be in good agreement with the hood measurements when plotted as a function of ϕ_g. However, the upper-layer CO concentrations in the front of the enclosure were approximately 50% higher than observed in the hood experiments, indicating that the GER concept was inadequate for predicting upper-layer concentrations for this position in the RSE.

Since it was not possible to make experimental measurements of velocity fields or mixing behavior within the RSE, a computational effort was initiated at NIST employing a three-dimensional k-ϵ model. [16] The commercial code used for these calculations was *FLOW3D*. [17] The experiment modeled was a 400 kW fire centered in the RSE. The calculated velocity profiles indicated that strong recirculation patterns develop within the enclosure, and that mixing within the RSE is not uniform. One surprising result of the calculations was that the flow patterns resulted in significant transfer of air directly from the lower layer into the upper layer in a region located behind the fire plume. The flow field rapidly transported the enriched-oxygen upper-layer gases to the front of the enclosure. A detailed chemical-kinetic model in conjunction with simplified models of mixing (either plug-flow or perfectly stirred reactor) has shown that air which is mixed into a rich upper layer reacts to generate primarily CO in preference to CO_2. [18] The elevated concentrations of CO in the front of the RSE (as compared with the corresponding hood experiment) are therefore attributed to direct mixing of air into the upper layer with subsequent reaction to generate CO.

An analysis of full-scale fire tests has shown that the levels of CO generated by wood fires is much higher than predicted by the hood experiments. [19] Previous experiments have suggested that high concentrations of CO can be generated by high-temperature wood pyrolysis in oxygen-depleted atmospheres such as observed in the rich upper layers in the RSE. [20] It was hypothesized that increased production of CO could result from pyrolysis of wood or other oxygen-containing fuels located in such an environment. The results shown in Fig. 4 confirm this hypothesis. Differences between the CO concentrations observed in the front and rear of the RSE are attributed to differences in the residence times for combustion gases in the two locations. The k-ϵ modeling indicated that a recirculation zone develops in the rear which leads to much longer residence times in this region of the RSE. As a result, gases generated by the pyrolysis build up to

the higher levels observed. It seems likely that the extremely high concentrations of CO observed in many full-scale fire tests involving wood results from the pyrolysis in the low-oxygen, high-temperature environments generated by underventilated enclosure fires. A similar behavior might be expected for any fuel which contains oxygen.

The findings of this study show that there are at least two important mechanisms for CO generation in enclosure fires in addition to the CO formation mechanism investigated in the hood and VPISU enclosure experiments (quenching of a fire plume within a rich upper layer). The first involves direct entrainment of air into an upper layer by fire- induced flows within the enclosure followed by rapid chemical reaction to generate CO. The second formation mechanism is important when fuels containing oxygen are located in a rich, high-temperature upper layer where pyrolysis results in the generation of CO.

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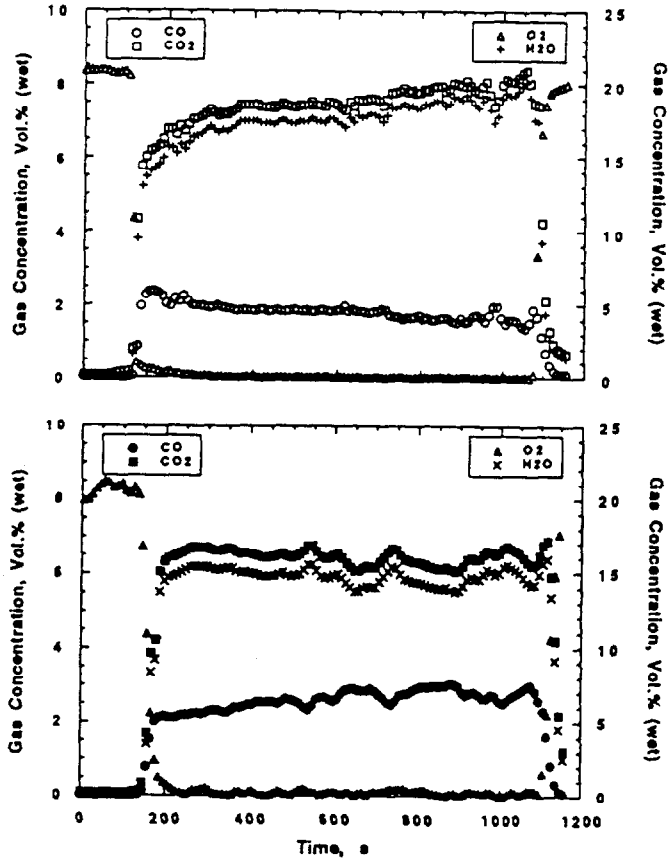

Fig. 1 CO, CO_2, O_2, and calculated H_2O concentrations (wet percents) plotted as a function of time for a 500 kW natural gas fire in the RSE. Measurements in the upper layer for the front (solid symbols) and rear (open symbols) are shown.

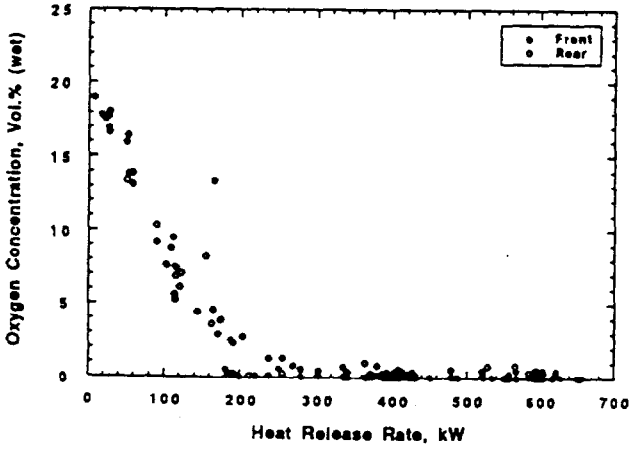

Fig. 3 O_2 concentrations observed during pseudo-steady state burning of natural gas fires in the RSE are plotted as a function of nominal heat release rate. Measurement positions were in the front and rear.

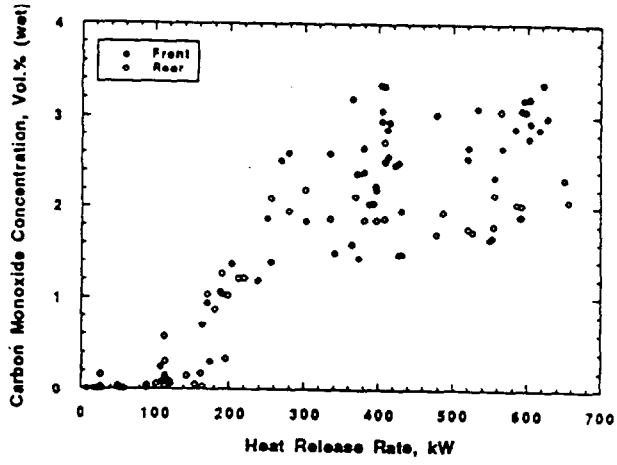

Fig. 2 CO concentrations observed during pseudo-steady state burning of natural gas fires in the RSE are plotted as a function of nominal heat release rate. Measurement positions were in the front and rear of the RSE.

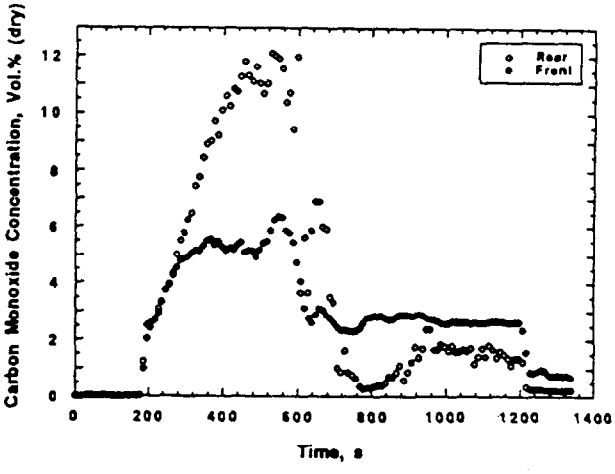

Fig. 4 CO concentrations for probe locations in the front and rear of the RSE are plotted as a function of time for a burn with the RSE lined with wood on the ceiling and upper walls. The nominal heat release rate for the natural gas fuel was 600 kW.