

Limitations of the Global Equivalence Ratio Concept
for Predicting CO Formation in Room Fires

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ABSTRACT

Recent experimental and modeling efforts designed to characterize the formation of carbon monoxide (CO) in enclosure fires which were funded by or performed at the Building and Fire Research Laboratory (BFRL) of the National Institute of Standards and Technology (NIST) are summarized. The findings are used to assess the conditions for which the Global Equivalence Ratio Concept can be used to predict the generation of CO and other combustion gases by enclosure fires.

1. INTRODUCTION

Roughly two thirds of all deaths resulting from enclosure fires can be attributed to the presence of 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]

Much of the effort over the past four years has been focused on answering the following question:

Can the generation behavior of CO observed in hood experiments designed to model two-layer burning be extended to predict CO generation in actual enclosure fires?

This paper summarizes recent experimental and theoretical investigations. The results are used to assess the conditions for which correlations of major combustion products (with a particular focus on CO) with global equivalence ratio in the hood experiments can be used to predict the generation behavior of these gases in enclosure fires.

2. THE GLOBAL EQUIVALENCE RATIO CONCEPT

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 the laboratory. Such experiments are intended to be 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. Experiments showed that there is very little direct mixing of air from the laboratory into the hood "upper layer". The mass ratio of fuel and air entering the hood is given by the ratio of the flow rate of the fuel and the entrainment rate of air into the fire plume. Usually, such experiments are allowed to come into a steady state for which the upper-layer combustion gases have the same fuel-to-air mass ratio as the fire plume. The mass ratio in the upper layer is 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 combustion gases in the upper layer can be correlated in term of the GER. The correlations are found to be independent of nominal fire heat release rate and burner/upper-layer separation. A dependence of combustion product concentrations on upper-layer temperature has been identified as discussed below. The correlations also depend on the fuel. Beyler has shown that the level of CO generated is correlated with fuel type (e.g., alkanes or alcohols). [5],[6],[7] Morehart et al. have reported an experiment in which air was introduced directly to the upper layer as well as by the fire plume. [9],[10],[11] In this case the GER was reduced from the plume equivalence ratio. Remarkably, the same correlations of combustion gases with the GER were found as for the case where the only source of gasses in the upper layer was the fire plume.

Figures 1 and 2 show the correlations obtained by Morehart et al. [9] for CO and O₂ mass fractions in the hood above a natural gas fire. The collapse of the concentration measurements to a single curve is excellent. Data from a similar experiment by Toner [8] for the same fuel are included on the figure. Systematic differences are obvious. Morehart has analyzed the differences and attributes them to the higher temperatures present in the upper layer for the Toner experiment. [9] In the lower temperature measurements, CO (a product of incomplete combustion) is found for lean mixtures ($\phi_g < 1.0$). For rich conditions ($\phi_g > 1.0$), oxygen and fuel exist together in the upper layer. At the higher temperatures, oxygen concentrations for rich conditions are nearly zero indicating more complete combustion. Similarly, the CO concentrations observed by Toner are reduced for lean conditions.

The existence of the correlations shown in Figs. 1 and 2 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 in such fires. This point is addressed below. One factor which must be considered is the temperature differences between the upper layers in the hood experiments (< 700 K for most experiments) and enclosure fires (> 1000 K and as high as 1300 K for the fully-developed fires generally associated with smoke-inhalation fatalities).

3. CHEMICAL-KINETIC MODELING

Pitts [12] modeled the reaction behavior of gases observed in the hood experiments of Morehart [9] for the higher temperatures characteristic of enclosure fires using a detailed chemical kinetic mechanism employing 31 species undergoing 181 reactions. Since the actual mixing and heat loss behaviors within the upper layer of a fire are difficult to characterize, models were employed which assumed infinitely fast (perfectly stirred reactor) and infinitely slow (plug-flow reactor) mixing. Calculations were done assuming no heat transfer (adiabatic) and full heat transfer (isothermal) to the surroundings.

Concentrations of combustion gases, taken directly from the hood experiments of Morehart [9] for natural-gas fuel having a range of $\phi_g = 0.5 - 2.83$, were used as initial inputs for the models. The reaction behavior was calculated as a function of residence time (0-20 s) for a range of temperatures (700 - 1300 K). The calculations showed that the combustion gases in the hood become reactive at temperatures ≥ 800 K. Figure 3 shows calculated CO concentrations as a function of time over a range of temperatures for an isothermal plug-flow reactor with $\phi_g = 2.17$. At 700 K there is very little reaction in agreement with observations in the hood experiments. As the temperature is increased the CO concentrations begin to rise due to reactions within the rich combustion gases. The final concentration of CO achieved depends on the temperature with higher concentrations formed

at higher temperatures. Analysis showed that the temperature dependence is due to changes in the relative amounts of H_2 and H_2O generated by the oxidation of fuel.

For rich conditions, CO was much more likely to be generated than CO_2 . This is due to the fact that organic fuels are much more reactive with the important free radicals ($OH\cdot$, $HO_2\cdot$, and H atoms) than with CO. As a result, in the presence of fuel, radical concentrations are suppressed and partial oxidation to CO occurs slowly. Even for lean conditions, it was observed that any existing fuel would first be oxidized relatively slowly to generate CO, H_2 , and H_2O , and then, once the fuel was depleted, the CO and H_2 would rapidly react to form fully oxidized products.

Mixing conditions were found to have very little effect on reaction behavior. Heat transfer did play a role due to the increased temperatures within the reactors for adiabatic conditions. However, it was possible to understand the changes in product distributions in terms of the variations in reaction behavior with increasing temperature observed in the isothermal calculations.

4. CO GENERATION IN ENCLOSURE FIRES

Ongoing projects at Virginia Polytechnic Institute and State University (VPISU, sponsored by BFRL) [13] and NIST [14] are investigating the generation of CO in model compartments. The facility at VPISU is especially designed to generate an environment similar to that of the hood experiments described earlier. Air enters through long slots in the floor of the enclosure and combustion products are exhausted through a vent in one side. Such a configuration ensures a well defined two-layer environment. Products of combustion were shown to be well mixed in the upper layer. 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. Fuels which have been burned are hexane, PMMA, wood, and polyurethane foam containing 45% by weight of inert filler.

Figure 4 shows a time record for a hexane-fueled fire. Gas measurements refer to upper-layer concentrations. A pseudo-steady state period of burning with a GER of 2.9 was observed. It can be seen that as the fire grew, the O_2 concentration dropped to zero, and the CO concentration grew to 2.4 volume percent. Figure 5 shows CO yields (g CO generated per g fuel consumed) as a function of GER for measurements in hexane-fueled fires. Results from Beyler's hood experiments are included for comparison. For $\phi_g < 1.5$ yields of CO observed for the fire are less than those measured in the hood experiments. At higher ϕ_g the yields of CO for the fire appear to be slightly higher, but in general are in good agreement with the hood experiments. Upper-layer temperatures in the enclosure fires were several hundred degrees higher than in the hood experiments. The shifts in CO yield at the lower ϕ_g are the result of the temperature effect discussed above. Results for the other fuels investigated by Gottuk et al. were similar. [13] The VPISU experiments show that the hood experiments provide good estimates for the upper-layer composition within enclosures under rich burning conditions when the temperature effect is accounted for.

A facility has also been developed at NIST for the investigation of CO formation in enclosure fires. [14] This system, dubbed the reduced-scale enclosure (RSE), is 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. Standard

instrumentation for RSE fire characterization consisted of arrays of thermocouples and two banks of analyzers containing a paramagnetic analyzer for oxygen and non-dispersive infrared (NDIR) analyzers for CO and CO₂. 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], was used to measure the local equivalence ratio of the combustion gases extracted from the enclosure. Measurements of gas properties were made for samples extracted from the RSE by stainless-steel probes.

The fuel source for the fires was a 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. Fires were burned long enough to achieve pseudo-steady state burning. The time behaviors of the concentrations of O₂, CO, CO₂, and H₂O in the front and rear of the enclosure are shown in Fig. 6 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 7 and 8 show concentrations of CO and O₂ measured in the front and rear upper layers as a function of HRR. The CO concentrations begin to increase for HRR > 200 kW, and the levels then 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. [13], the upper layer is not well mixed. Oxygen concentrations fall with increasing HRR rate and approach zero near the HRR of 200 kW where the CO concentrations start to increase.

Measurements using the ϕ -meter showed that a HRR of 200 kW roughly corresponds to a GER of 1. 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. Concentrations of CO, CO₂, and O₂ as a function of the GER in the rear of the RSE were in good agreement with those of Toner et al. [8] for a hood experiment using the same fuel. CO concentrations in the front of the RSE were considerably higher than observed in the hood experiments.

Fires were burned in the RSE for which the doorway was narrowed to 1 cm. Due to the considerably reduced ventilation, fires were much smaller with lower upper-layer temperatures (< 700 K). Under these conditions, the upper layers were much more uniform than with the open door, and the concentrations of CO, CO₂, and O₂ as a function of GER were in good agreement with the hood measurements of Morehart et al. [9]. In particular, the formation of CO for lean conditions was observed and significant concentrations of O₂ were found in the upper layer for $\phi_g > 1$.

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. [16] Experiments suggested that high concentrations of CO could be generated by high-temperature wood pyrolysis in oxygen-depleted atmospheres. [17] It was hypothesized by the author that increased production of CO could result from pyrolysis of wood or other oxygen-containing fuels located in the oxygen-depleted, high-temperature upper layers characteristic of fully developed enclosure fires. In order to test this hypothesis, the upper walls and ceiling of the RSE were lined with plywood. Figure 9 shows the concentration 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. [18] During the period when the wood was in the upper layer (the wood fell off the walls and ceiling at ≈ 650 s), extremely high levels of CO were detected in the rear of the RSE and the concentrations in the front were elevated $\approx 50\%$. These results show that pyrolysis of oxygen-containing solid fuels in an upper layer of an underventilated enclosure fire can lead to significant generation of CO.

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. [19] The commercial code used for these calculations was *FLOW3D*. [20] The walls were assumed to remain at a constant temperature and heat losses were approximated by assuming that a fixed fraction of the heat release was loss by conduction and/or radiation. Combustion was simulated using the Eddy Breakup Model [21] where the degree of combustion is controlled solely by the rate of mixing of fuel and oxidizer. Burning was assumed to be complete and to occur instantaneously when fuel and air were mixed. Note that this model does not allow modeling of CO formation or other products of incomplete combustion.

The experiment modeled was a 400 kW fire centered in the RSE. The calculated velocity profiles indicate that strong recirculation patterns develop within the enclosure, and that mixing within the RSE is far from uniform. One surprising result of the calculations is that the flow patterns lead to significant transfer of air directly from the lower layer into the upper layer in a region located behind the fire plume. The flow fields rapidly transport the enriched-oxygen upper-layer gases to the front of the enclosure. The chemical-kinetic modeling discussed earlier suggests that such entrained air reacts to generate CO, H₂, and H₂O. This conclusion provides an explanation for the observation of higher CO levels in the front of the RSE than predicted based on the hood experiments.

5. CRITERIA FOR THE APPLICATION OF THE GER CONCEPT TO ENCLOSURE FIRES

The findings summarized above allow the conditions for which the application of the GER concept to the prediction of combustion gas formation in enclosure fires is appropriate to be assessed. These conditions can be summarized as:

Use of GER Appropriate:

- 1) Fires for which the upper-layer temperature is less than 700 K.
- 2) Fires for which the upper layer is lean and very hot (> 900 K).
- 3) Fires for which the only route for oxygen (air) to enter the upper layer is through the fire plume and the upper layer is very hot (> 900 K).

Use of GER Inappropriate:

- 1) Fires having slightly lean or rich upper layers and intermediate temperatures (700-900 K)
- 2) Fires for temperatures greater than 900 K for which oxygen (air) enters a rich upper layer directly.
- 3) Fires which generate rich, high-temperature upper layers and which have solid fuels capable of pyrolysis located in the upper layer.

Analysis of the types of enclosure fires which are responsible for the majority of smoke-inhalation deaths suggests that these fires usually burn underventilated, are quite intense, and have achieved flashover. Wood and/or other polymeric materials are often located in the upper areas of the compartments. As a result, for the types of fires most likely to kill people, it is concluded that the GER concept alone will not be adequate to predict the production of CO.

6. REFERENCES

1. B. Harwood and J. R. Hall, *Fire J.* **83** (1989) 29.
2. W. A. Harland and R. A. Anderson, "Causes for Death in Fires," *Proceedings: Smoke and Toxic Gases From Burning Plastics*, London, England, Jan. 6-7, 1982, pp. 15/1-15/19.

3. V. Babrauskas, B. C. Levin, R. G. Gann, M. Paabo, R. H. Harris, Jr., R. D. Peacock, and S. Yusa, National Institute of Standards and Technology Special Publication 827 (1991).
4. W. M. Pitts, NISTIR 89-4185 (1989).
5. C. L. Beyler, *Development and Burning of a Layer of Products of Incomplete Combustion Generated by a Buoyant Diffusion Flame*, PhD Thesis, Harvard University (1983).
6. C. L. Beyler, *Fire Safety J.* **10** (1986) 47.
7. C. L. Beyler, *Fire Safety Science--Proceedings of the First International Symposium*, Hemisphere: New York (1991) 431.
8. S. J. Toner, *Entrainment, Chemistry and Structure of Fire Plumes*, PhD Thesis, California Institute of Technology (1986).
9. J. H. Morehart, *Species Produced in Fires Burning in Two-Layered and Homogeneous Vitiated Environments*, PhD Thesis, California Institute of Technology (1990).
10. E. E. Zukoski, S. J. Toner, J. H. Morehart, and T. Kubota, *Fire Safety Science--Proceedings of the First International Symposium*, Hemisphere: New York (1988) 295.
11. E. E. Zukoski, J. H. Morehart, T. Kubota, and S. J. Toner, *Combust. Flame* **83** (1991) 325.
12. W. M. Pitts, "Reactivity of Product Gases Generated in Idealized Enclosure Fire Environments," *Twenty-Fourth Symposium (International) on Combustion*, to appear.
13. D. T. Gottuk, R. J. Roby, and C. L. Beyler, to appear in *J. Fire Protection*.
14. N. P. Bryner, E. L. Johnsson, and W. M. Pitts, "Carbon Monoxide Production in Compartment Fires: Reduced-Scale Enclosure Test Facility," National Institute of Standards and Technology Internal Report, to appear (1992).
15. V. Babrauskas, W. J. Parker, G. W. Mulholland, and W. H. Twilley, "The Phi-Meter: A Simple, Fuel-Independent Instrument for Monitoring Combustion Equivalence Ratio," to be submitted for publication.
16. G. W. Mulholland, "Position Paper Regarding CO Yield," Letter report to Richard G. Gann, Center for Fire Research (June 16, 1988).
17. V. Arpiainen and M. Lappi, *J. Anal. Appl. Pyrolysis* **16** (1989) 355.
18. W. M. Pitts, N. P. Bryner, and E. L. Johnsson, unpublished work.
19. W. Davis, Manuscript in preparation.
20. CFD Department, AEA Industrial Technology, Harwell Laboratory, Oxfordshire, U. K. Harwell-FLOW3D Release 2.3: Users Manual, July, 1990.
21. D. B. Spalding, *Sixteenth Symposium (International) on Combustion* (1977) 1657.

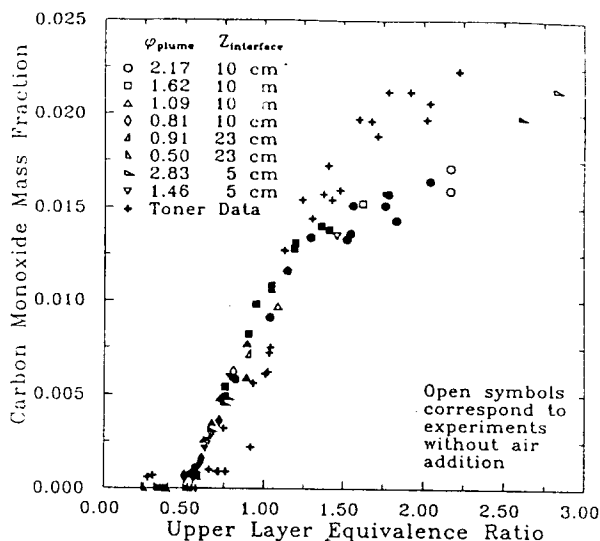


Fig. 1 CO mass fractions observed by Morehart [9] in the combustion gases trapped in an upper layer above natural gas fires are plotted as a function of ϕ_p . Filled symbols correspond to cases where $\phi_p \neq \phi_g$. The results of similar measurements by Toner [8] are included for comparison. Figure reproduced from [9].

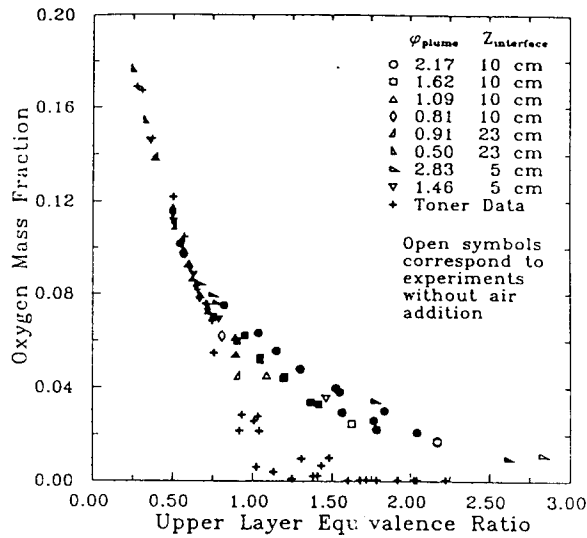


Fig. 2 O_2 mass fractions observed by Morehart [9] in the combustion gases trapped in an upper layer above natural gas fires are plotted as a function of ϕ_p . Filled symbols correspond to cases where $\phi_p \neq \phi_g$. The results of similar measurements by Toner [8] are included for comparison. Figure reproduced from [9].

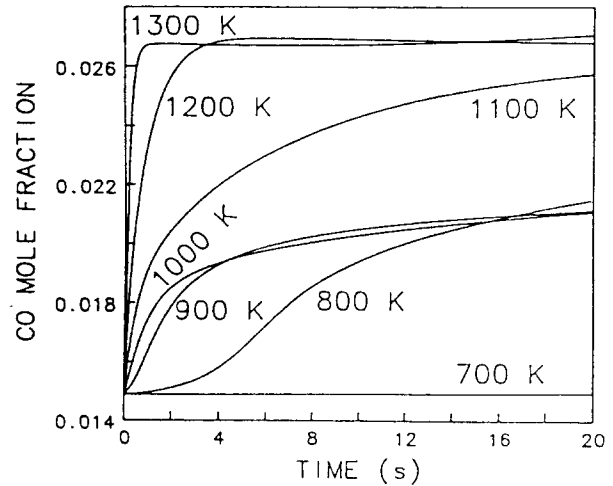


Fig. 3 Calculated carbon monoxide mole fractions as a function of time for an isothermal plug-flow reactor for the temperatures indicated. $\phi_g = 2.17$. Initial concentrations taken from Morehart. [9]

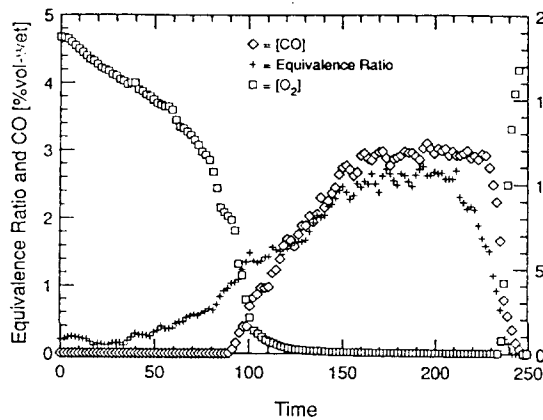


Fig. 4. Equivalence ratio and CO and O_2 volume percents (wet) are shown as a function of time for a hexane-fueled fire in the VPISU facility. The development of the fire and the attainment of a pseudo-steady state are evident. Figure provided by Dan Gottuk.

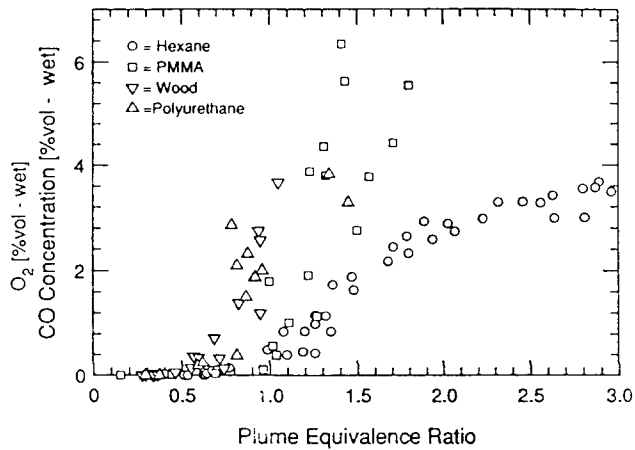


Fig. 5 Carbon monoxide concentrations observed during steady-state burning in the VPISU facility are plotted as a function of ϕ_p for the four fuels investigated. Figure provided by Dan Gottuk.

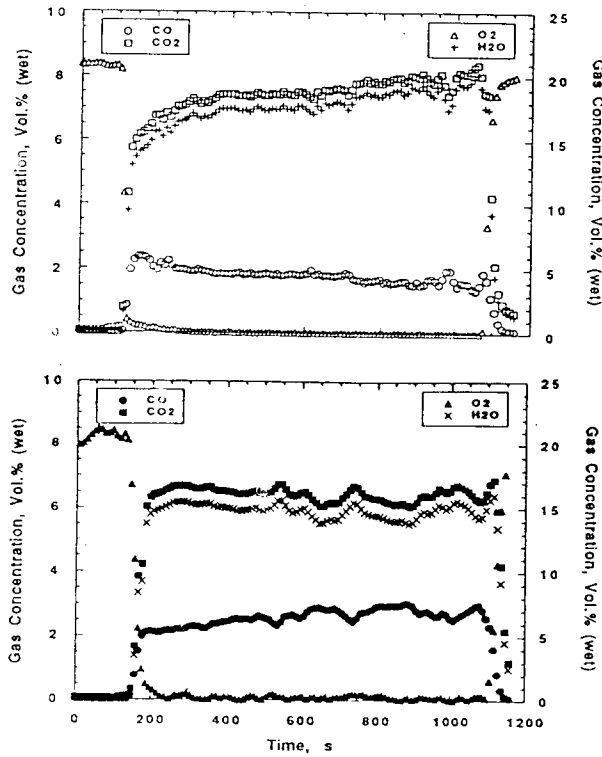


Fig. 6 CO, CO₂, O₂, and calculated H₂O concentration (wet percents) plotted as a function of time for a 500 kW natural gas fire in the RSE. Measurements in the upper layer for the front (solid symbols) and rear (open symbols) are shown.

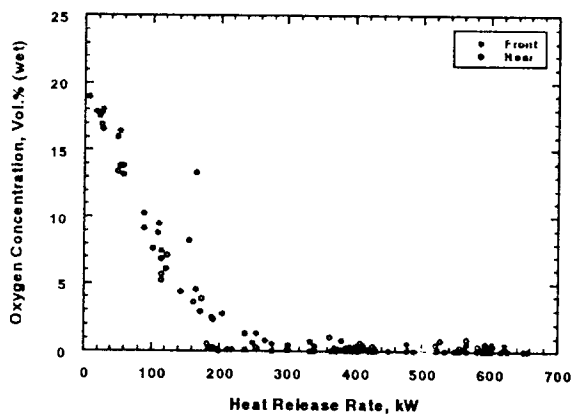


Fig. 8 O₂ concentrations observed during pseudo-steady state burning of natural gas fires in the RSE are plotted as a function of nominal heat release rate. Measurement positions were in the front and rear.

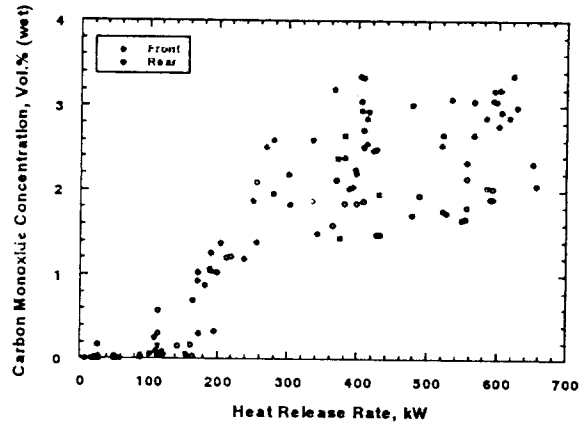


Fig. 7 CO concentrations observed during pseudo-steady state burning of natural gas fires in the RSE are plotted as a function of nominal heat release rate. Measurement positions were in the front and rear of the RSE.

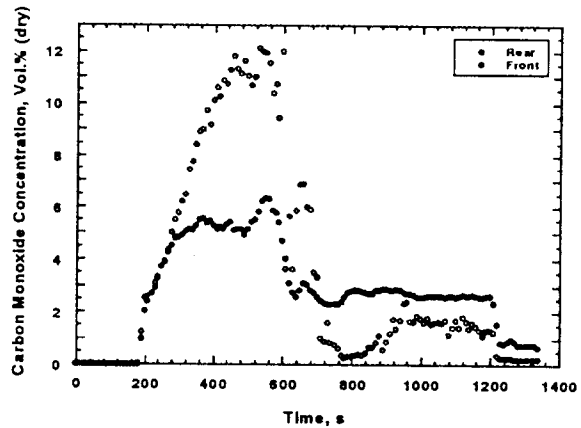


Fig. 9 CO concentrations for probe locations in the front and rear of the RSE are plotted as a function of time for a burn with the RSE lined with wood on the ceiling and upper walls. The nominal heat release rate for the natural gas fuel was 600 kW.