

TOXIC YIELD

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Introduction

It is generally recognized that the vast majority of deaths associated with accidental enclosure fires are due to smoke inhalation. Older reviews of autopsy results suggested that the fraction was on the order of 2/3.^{1,2} In the United States there is evidence that this number has been growing in recent years and is approaching 3/4.³ Autopsy results have also shown that the vast majority of these fire victims have carboxyhemoglobin levels in their bloodstreams sufficient to induce incapacitation or death. This has led many researchers to conclude that carbon monoxide (CO) is the dominant toxicant present in fire gases.^{4,5,6} It is recognized that the elevated carbon dioxide (CO₂) levels (which result in increased respiration rates) and depressed oxygen (O₂) levels associated with the fire gases act together to increase the susceptibility of victims to CO asphyxiation. The importance of CO toxicity is highlighted by the conclusion that most victims in the United States are overcome at locations remote from the room of fire origin.⁴

In recognition of the central role that CO plays in smoke inhalation fire deaths and the fact that mechanisms for CO formation in fires were poorly understood, the National Institute of Standards and Technology initiated an investigation of CO formation in fires over a decade ago.⁷ In the interim, significant progress has been made on identifying the formation mechanisms for CO within an enclosure containing a fire. As will be discussed, additional investigation is necessary to provide an adequate understanding of the subsequent reaction and transport of CO upon exiting the fire enclosure.

This paper focuses on the current understanding of CO formation mechanisms in real-scale fires with a particular emphasis on post-flashover generation. This emphasis is justified by our current understanding of the central role of CO in fire toxicology as well as the fact that during the past twenty years CO formation in fires has received a great deal of research attention, and significant progress has been made. It will become evident that an understanding of the formation of CO in real-scale fires requires consideration of the unique fluid dynamics and mixing associated with fires in enclosures as well as the kinetics and thermodynamics associated with the formation and destruction processes for CO in fire environments. An extensive review article by this author summarizing research on CO formation in fires up to 1994 is available.⁸

Hood experiments and the global equivalence ratio (GER) concept

Much of the current understanding of CO formation in fires has its origins in relatively small-scale experiments that were originally designed to investigate entrainment into fire plumes. Ultimately, it was recognized that such experiments generate environments similar to those present in the upper layer of a compartment fire burning under flashover conditions. Among these early studies are the ingenious "hood" experiments of Beyler^{9,10} and Zukoski and coworkers.¹¹⁻¹⁴ These researchers placed hoods above laboratory fires such that the products of combustion were captured. By varying the height of the hood above the fire base and allowing the system to come to a steady state, it was possible to vary the composition of fire gases in the hood. When the hood was located well above the top of a fire only the combustion gases generated in the fire plume and additional entrained air were collected. However, when the hood was lowered below the top of the flame, insufficient air for complete combustion was entrained

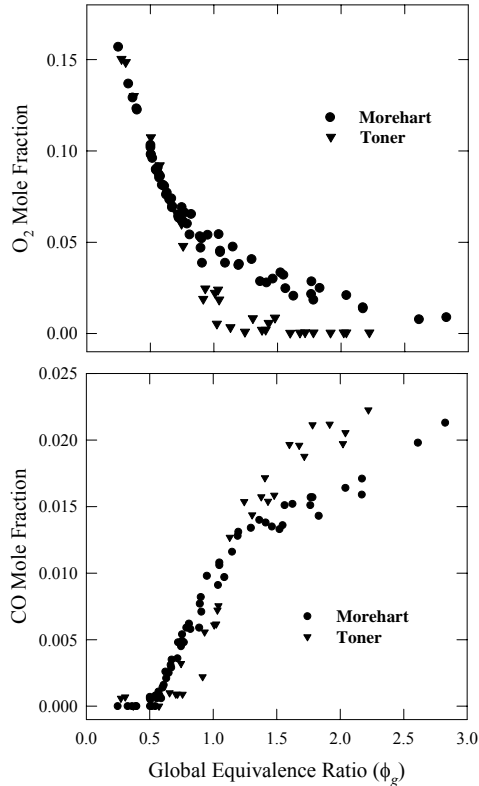


Figure 1. Mole fractions of O₂ and CO measured during the hood experiments of Toner [11] and Morehart [12] are plotted as functions of the observed global equivalence ratios in the hood. The fuel was natural gas in both cases.

within the fire plume, and increased concentrations of products of incomplete combustion, including CO, began to appear. The concentrations of hood gases such as CO, CO₂, and O₂ were measured and were found to be strongly correlated with a parameter referred to as the global equivalence ratio (ϕ_g) or GER, which is defined as:

$$\phi_g = \frac{\text{Mass in the upper layer derived from fuel}}{\text{Mass in the upper layer derived from air}}, \quad (1)$$

where ϕ_s is the fuel-to-air ratio required for complete combustion of the hydrocarbon fuel to carbon dioxide and water. The existence of these correlations has been termed the “GER Concept”.

Figure 1 shows examples of such correlations obtained for O₂ and CO during hood experiments using natural gas as the fuel.^{11,12} It has been found that the concentrations of CO measured in hood experiments for high global equivalence ratios depend somewhat on the fuel used.⁹⁻¹⁴ However, when the measurements are converted to units of mass of CO generated per mass of fuel consumed, they are found to cluster near a value of 0.2 kg/kg.¹⁰ This value is close to that

recommended by Mulholland as being typical of real-scale fires based up a review of a number of large-scale fire tests.¹⁵

As is evident in Fig. (1), the various hood experiments have shown that high concentrations of CO are generated when a burning fire plume enters an upper layer that has insufficient oxygen to allow complete combustion to fully oxidized products. However, as can also be seen in Fig. (1), it has also been found that the dependence of upper-layer gas concentrations on ϕ_g could vary between different hood experiments using the same fuel. Ultimately, it was shown that these variations were correlated with the temperature of the gases trapped in the hood above the fire. At lower upper-layer temperatures, it was found that fuel and/or its breakdown products (including CO) and O₂ could coexist in the hood over a significant range of lean and rich conditions, but that as the upper-layer temperature was increased the amount of O₂ present tended to decrease and the amount of CO formed increased. With further increases in temperature the degree of reaction was such that fuel and its breakdown products and O₂ could no

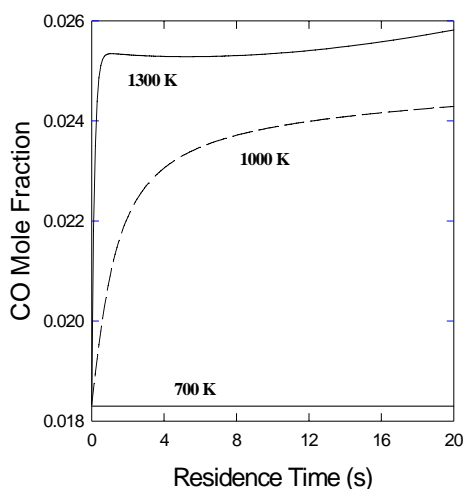


Figure 2. The calculated variation of CO volume fraction is shown as a function of time for an isothermal plug-flow reactor held at the indicated temperatures.¹⁷ The volume fractions at time = 0 s are taken from the hood measurements of Morehart¹² for a natural gas fire with $\phi_g = 2.61$: H₂, 0.0193; O₂, 0.0078; N₂, 0.5950; CH₄, 0.1148; CO, 0.0182; CO₂, 0.0675; H₂O, 0.1654; C₂H₂, 0.0028; C₂H₆, 0.0022; Ar, 0.0070.

longer coexist and only O₂ was present for $\phi_g < 1$ and only fuel was present for $\phi_g > 1$. These effects are evident in Fig. (1) when it is noted that the upper-layer gas temperatures in Toner's experiments were 100 °C to 300 °C higher for a given ϕ_g than observed by Morehart.

Detailed chemical-kinetic modeling of upper-layer gas reactivity

Initial attempts to understand the temperature dependence of the hood experiments were based on thermodynamic arguments for which it was assumed that the combustion gases in a hood come into thermodynamic equilibrium at the temperature of the hood gases.¹⁶ However, concentrations of the various species were inconsistent with this assumption. Detailed chemical-kinetic modeling calculations by Pitts^{17,18} and later by Gottuk et al.¹⁹ showed why the assumption of thermodynamic equilibrium is inappropriate and also provided a general understanding for the observed temperature effects in hood experiments. In these calculations the reaction behaviors of gas mixtures typical of those observed in the hood experiments were calculated as a function

of temperature. At low temperatures the reaction rates of rich mixtures containing fuel and oxygen were very slow, i.e., the compositions were “frozen” at levels very different from those predicted thermodynamically. As the temperature was increased, the reaction rates increased to a point where the reaction times became comparable to residence times expected in the hood experiments, but the concentrations attained at long times were still far from their equilibrium values. Significantly, the modeling results showed that when both organic fuel molecules and oxygen were present the fuel molecules were predominantly oxidized to CO and that rapid conversion of CO to CO₂ would only occur when the organic fuel molecules were depleted to very low concentrations. These effects can be seen

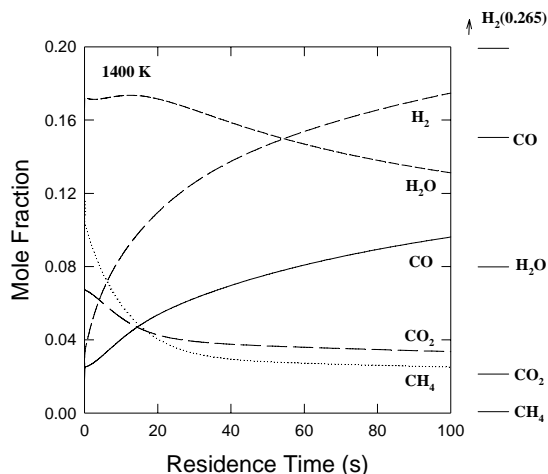


Figure 3. Calculated time behaviors for H₂, CO, H₂O, CO₂, and CH₄ are shown as a function of residence time for a plug-flow reactor held at 1400 K. The volume fractions at time = 0 s are taken from the hood measurements of Morehart¹² for a natural gas fire with $\phi_g = 2.61$ and are listed with Fig. 2. Equilibrium concentrations for 1400 K are shown on the right-hand side of the plot

in Fig. (2) where the calculated volume fraction of CO as a function of time is shown for a plug-flow reactor held at constant temperatures of 700 K, 1000 K, and 1300 K. The initial conditions were taken from the experimental hood results of Morehart for $\phi_g = 2.61$.¹²

The modeling results indicated that rich gas mixtures of hood gases only begin to approach thermodynamic equilibrium when the temperature is increased to values on the order of 1400 K. Figure (3) shows the calculated reaction behavior of the same initial mixture of gases used for the results shown in Fig. (2), but for a reactor temperature of 1400 K. At this high temperature a slow conversion of H₂O and CO₂ to H₂ and CO is predicted to take place by the water-gas shift reaction. Under these conditions, very high concentrations of CO can be generated for rich flame gas mixtures.

Effect of air vitiation on carbon monoxide formation

Additional insights into the mechanisms responsible for CO generation in fires were provided by experiments reported by Mulholland et al.²⁰ and Morehart et al.^{21,22} These researchers considered the effects of vitiation of the air on the amount of CO generated. Combustion in vitiated air is often cited as a possible mechanism for the generation of high levels of CO. These studies indicated that this is not the case. While vitiation of the oxidizer leads to minor increases

in CO formation, as long as sufficient oxidizer is available for complete combustion, these increases are small when compared to those observed when a combusting fire plume is quenched upon entering a rich upper layer.

Carbon monoxide formation in reduced-scale enclosure fires

The hood experiments obviously represent a highly idealized model for an enclosure fire since burning occurs in an open laboratory. It was necessary to investigate whether the conclusions were appropriate for actual enclosure fires and, in particular, whether the GER concept could be used to predict upper-layer concentrations in real fires. The first step in this direction was provided by Gottuk et al.^{23,24} who investigated the burning of hexane, polymethyl methacrylate (PMMA), wood, and polyurethane in a 1.2 m × 1.2 m × 1.5 m enclosure especially designed to have a separate air inlet at the bottom and an exhaust outlet near the top. In this way it was possible to measure directly the mass flow rate of air entering the enclosure as well as the mass loss rate of fuel. These measurements allowed the GER to be calculated dynamically. Experiments showed that the upper layer formed within the enclosure was well mixed. Concentrations of major flame gases in the upper layer were measured and plotted as a function of the GER calculated using the air and fuel mass flow rates. These concentrations fell on well-defined curves having similar shapes to those previously identified in the hood experiments. Beyler^{9,10} had reported hood experimental results for hexane, PMMA, and wood that were compared directly to the enclosure results. Small shifts in the data for the two systems were noted. Consistent with the findings in the hood experiments, these shifts were to be expected since the upper-layer temperatures were considerably higher for the enclosure fires. These findings indicated that the use of the GER concept could be extended to enclosure fires.

Bryner et al.^{8,25} studied natural-gas fires in a 40%-scale model of a standard room widely used in fire testing.^{26,27} This facility is referred to as the reduced-scale enclosure (RSE). The dimensions were 1.0 m × 1.0 m × 1.5 m and included a single doorway designed to scale the ventilation relative to the real-scale enclosure. The mass flow rate of natural gas was metered. In order to calculate the GER for the upper layer it was necessary to have a measure of the mass flow rate of air entering the room through the doorway. This was obtained using thermocouple measurements in conjunction with an algorithm supplied by Janssens and Tran²⁸ that employs temperatures measured within the enclosure and along the doorway vertical centerline to calculate the mass flow rates into (\dot{m}_i) and out of (\dot{m}_o) the doorway. The resulting equations are:

$$\dot{m}_i = C_i W_d \rho_\infty T_\infty \sqrt{2g} \int_0^{z_N} \sqrt{\frac{1}{T_d(z')}} \left| \int_{z'}^{z_N} \left(\frac{1}{T_i(z'')} - \frac{1}{T_\infty} \right) dz'' \right| dz' \quad (2)$$

and

$$\dot{m}_o = C_o W_d \rho_\infty T_\infty \sqrt{2g} \int_{z_N}^{H_d} \sqrt{\frac{1}{T_d(z')}} \left| \int_{z_N}^{z'} \left(\frac{1}{T_i(z'')} - \frac{1}{T_\infty} \right) dz'' \right| dz', \quad (3)$$

where C_o and C_i are flow coefficients, W_d is the doorway width, ρ_∞ is the ambient air density, T_∞ is the ambient temperature, g is the gravitational constant, z_n is the height of the neutral plane, H_d is the doorway height, T_d is the temperature in the doorway, T_i is the temperature inside the room, and z is the height above the floor. The equation is solved iteratively by varying z_n while requiring mass conservation under the assumption that the total mass flow through the doorway is not changing with time so that

$$\dot{m}_o = \dot{m}_i + \dot{m}_f, \quad (4)$$

where \dot{m}_f is the fuel mass flow rate.

Note that this approach assumes that any air entering through the enclosure doorway ultimately mixes with the upper-layer combustion gases before exiting the enclosure. As will be discussed shortly, a coding error was made in the implementation of the algorithm that resulted in an overestimate of the air mass flow rate by a factor of 2.8. Some of the implications of this overestimate will be discussed shortly, but it is important to note that it does not invalidate the major conclusions with regard to CO formation mechanisms discussed here.

Measurements at various locations within the upper layer of the RSE indicated that concentrations of flame gases and the temperature varied somewhat in the layer, with higher temperatures and CO concentrations (for rich conditions) occurring in the front of the enclosure near the ceiling. Figure (4) shows an example of this behavior for CO volume fraction, for which concentrations recorded in the front of the layer are roughly 50 % higher than in the rear. Measurements recorded at locations near the ceiling in the front and rear of the RSE are plotted as functions of ϕ_g , calculated as outlined above using Eqs. (2)-(4) along with

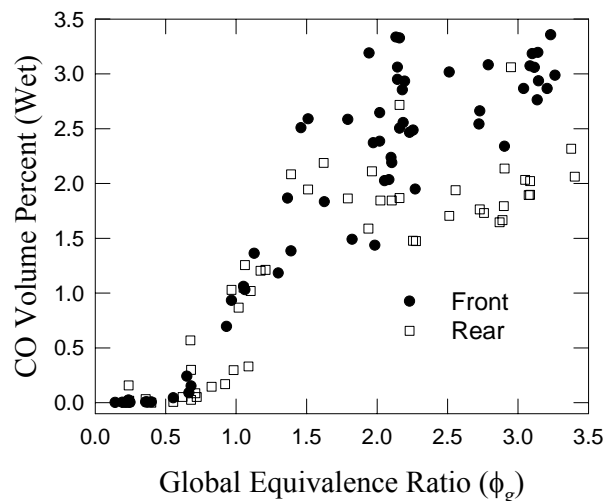


Figure 4. CO volume fractions recorded in the front (10 cm from front wall and ceiling, 29 cm from side wall) and rear (29 cm from rear and side walls, 10 cm from ceiling) of the RSE are plotted as a function of the GER calculated using Eqs. (2) – (4) and the known natural gas mass flow rate. The GER has not been corrected for a coding error (see text).

known natural gas mass flow rate. The measurements were recorded near the ends of the experiments when conditions had approached steady state. Note that these results have not been corrected for the coding error discussed above. Interestingly, measurements of the local equivalence ratio in the front of the upper layer using a meter especially developed for the purpose²⁹ were in found to be in excellent agreement with calculated values of ϕ_g . Values of the local equivalence ratio estimated from measured concentrations of CO₂ observed in the upper layer during periods when the GER was less than one, i.e., when complete combustion was expected, also agreed well with the GER.

The general dependence of CO volume fraction on ϕ_g for these two locations is similar to that observed in the hood experiments, e.g., see Fig. (1), using natural gas.¹¹⁻¹⁴ The rapid increases in CO volume fraction for the RSE occur near a calculated GER of 1 as expected. Closer comparison of Fig. (4) and Fig. (1) indicates shows that the CO concentrations measured in the rear of the upper layer for high values of ϕ_g are in much better quantitative agreement with the corresponding results for the hood experiments. The same was found to be true for O₂ and CO₂ concentrations. This observation suggests that an additional mechanism for CO formation, beyond the simple quenching of the fire plume upon entering a rich upper layer captured by the GER concept, must be active in the RSE. It was hypothesized that it was possible for air to mix directly into the upper layer without being entrained into the fire plume. Support for this hypothesis was available from a field-modeling study of the fire-induced flows in the RSE that indicated that entrainment of lower layer gases directly into the upper layer does occur and that this air is transported in a short time of to the front of the upper layer. Such entrained air is expected to mix rapidly with gases already present in the layer. For a highly underventilated upper layer at high temperatures, the mixed air and fuel are expected to react in a manner similar to that treated by the detailed chemical kinetic studies discussed earlier. Recall that the flow reactor results indicated that reaction under these conditions results almost exclusively in the formation of CO as opposed to CO₂.

Based on the results for reduced-scale enclosures discussed thus far it can be concluded that the use of the GER concept is appropriate for describing the formation of CO and other flame gases in enclosure fires. However, it is also apparent that additional formation mechanisms of CO are possible and do occur for certain conditions and that the composition of upper-layer gases can vary substantially with location. In order to accurately predict CO levels it will be necessary to incorporate these effects into models for CO formation.

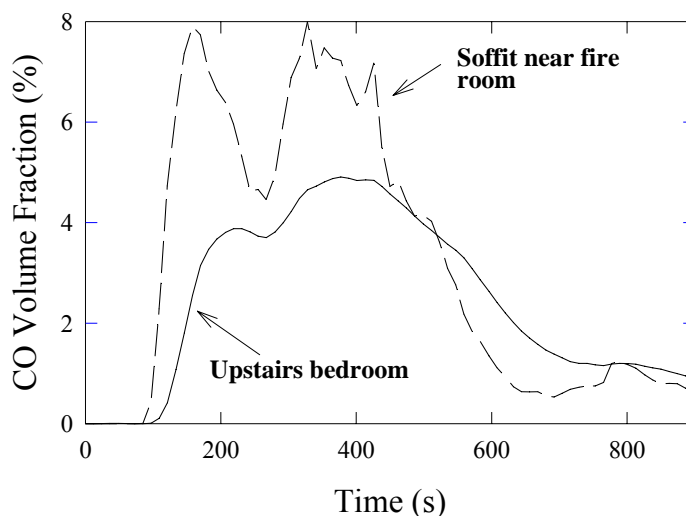


Figure 5. CO volume fractions recorded during a fire recreation involving a heavy loading of wood burning in a first-floor room of a two-story townhouse are shown.³⁰ Sampling positions were located just outside of the fire room and near the ceiling in an upstairs bedroom.

Formation of carbon monoxide due to anerobic pyrolysis of wood

Despite the success of the GER Concept in correlating the amount of CO and other flame gases generated in enclosure fires burning hydrocarbon fuels, it seemed to underpredict by a

substantial amount the levels of CO generated by real-scale fires involving wood. For example, during a full-scale fire recreation of a fatal fire that involved a heavy fuel loading of wood at the National Institute of Standards and Technology, Levine and Nelson³⁰ measured CO levels at two locations remote from the fire room that were more than twice as high as the levels recorded by Beyler⁹ in a hood experiment using wood as fuel (observed CO volume fraction of 3.2 %). Figure 5 shows a plot of the time variations of CO concentrations recorded during the fire recreation.

Pitts et al. speculated that wood, which contains oxygen as part of its molecular structure, was capable of generating CO directly by high temperature pyrolysis and that, if the pyrolyzate did not come into direct contact with oxygen, the additional CO would not be converted to CO₂.³¹ This hypothesis was tested by placing wood on the ceiling of the RSE and burning a natural gas fire of sufficient size to eliminate essentially all of the oxygen from the upper layer. For these conditions, concentrations of CO as high as five times greater than cases without the wood were observed as can be seen in Fig. (6). Later work by Lattimer et al. confirmed these findings and provided direct measurements of the mass loss rate for wood located in the upper layer.³²

Brief summary of carbon monoxide formation research since 1995

Several papers dealing with CO formation in fires in enclosures have appeared since the publication of the *Progress in Energy and Combustion Science* review.⁸ Bryner et al. reported measurements of flame gases in a real-scale ASTM standard room using natural gas as fuel and compared the findings with the results for the reduced-scale enclosure.³³ Upper-layer temperatures were found to be considerably higher than in the smaller enclosure. For underventilated burning, concentrations of CO in the larger room were observed to grow with time, reaching levels considerably higher than observed in the 40%-scale model RSE. An example of these results is shown in Fig. 7. Since the upper-layer temperatures observed in the full-scale room were significantly higher than recorded in the RSE, it was hypothesized that the temperatures within the upper layer were high enough for the flame gases to begin to react and approach thermodynamic equilibrium. The observed upper-layer temperatures in these fires continued to increase during a fire, consistent with the observed increases in CO concentration with time, and the measured values were comparable to the magnitudes predicted by the detailed chemical-kinetic modeling to be necessary for the upper-layer gases to begin to approach equilibrium (see Fig. 3).

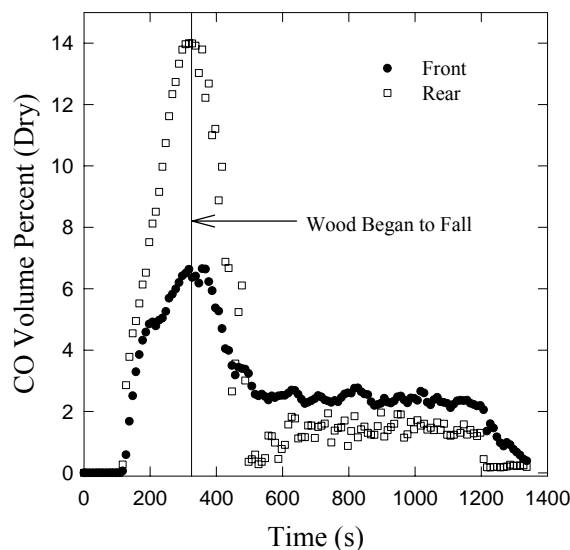


Figure 6. The volume fractions of CO recorded at locations in the front and rear of the upper layer during a nominally 600 kW natural gas fire in the RSE are plotted as a function of time. The ceiling and upper walls of the enclosure were lined with plywood.

Pitts summarized the findings of the studies discussed thus far and concluded that there are at least four distinct mechanisms for the formation of CO during enclosure fires.³⁴ These are: 1) quenching of a turbulent fire plume upon entering a rich upper layer, 2) mixing of oxygen directly into a rich, high-temperature upper layer with subsequent reaction, 3) pyrolysis of wood in high-temperature, vitiated environments, and 4) approach to full-equilibrium combustion product concentrations in a rich, high-temperature upper layer. The current knowledge concerning these formation mechanisms was collected into an algorithm designed to aid engineers in making predictions of the amount of CO generated during various burning periods of enclosure fires.

Very recently, Wieczorek et al. have reported measurements of CO in liquid-fueled pool fires in a 1/2-scale ISO 9705 enclosure having two different door widths.³⁵ The authors concluded that the flame gas concentrations generally correlated with the GER, but they found that there was a secondary effect of the doorway width on the results. This was attributed to a slight dependence of the combustion gas concentrations on the residence time for flame gases within the upper layer.

As mentioned above, researchers at NIST have recently discovered a numerical error in their implementation of Janssens and Tran's²⁸ algorithm for estimating the mass flow rates of air and combustion products through the doorway of an enclosure. The net result of this programming miscue is to reduce the magnitudes of previously calculated GERs by a factor of 2.8. Since the earlier results had indicated that the upper-layers of fires near the ceiling first became underventilated for GERs of approximately one (recall that estimates for the local equivalence ratio were consistent with this interpretation), the revised values suggest that this is actually taking place for GERs considerably less than one. This is likely associated with the observed variations in local equivalence ratio with upper-layer location discussed earlier. We are still investigating the implications of this discovery, but are confident that it doesn't invalidate our general conclusions concerning CO formation mechanisms. However, it does suggest that it may not be appropriate to calculate a global GER based simply on the fuel mass flow

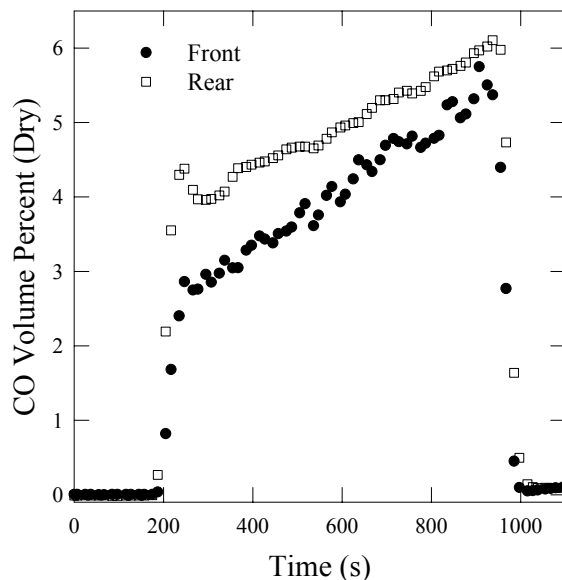


Figure 7. CO volume fractions recorded for locations in the front and rear of the upper layer of a nominally 2.7 MW natural gas fire burning in a full-scale standard enclosure.

rate and the air flow rate through the doorway. It appears as if a fraction of the air entering the doorway from the outside is not fully molecularly mixed with gases in the rich upper layer (either by entrainment into the fire plume or directly into the layer), and that a significant fraction exits the enclosure without encountering fuel under reactive conditions. Interestingly, Janssens and Tran discuss such a behavior in the context of a two-zone model.²⁸ If confirmed by additional study, this new enclosure fire behavior will require a redefinition of the enclosure GER to include only the mass of air that is directly mixed into the upper-layer combustion gases by entrainment into the fire plume and/or the upper layer.

Need for additional studies

The vast majority of studies of CO formation in fires have focused on its generation within the room of fire origin. However, it is clear that the subsequent reaction and transport of these gases are crucial to understanding the conditions under which victims are overcome at distances well removed from the fire. Preliminary studies of the behavior of rich flame gases containing high levels of CO upon exiting an enclosure into a corridor have been reported by Lattimer et al.³⁶ Studies of this type along with an improved ability to predict CO formation in an enclosure containing a fire will ultimately provide the understanding necessary to allow engineering estimates for the yield of this important flame toxicant in various fire scenarios.

The ultimate yield of CO in an enclosure fire results from complex interactions between flow and mixing, thermodynamics, and chemical kinetics. The studies summarized here have allowed us to begin to unravel these complex interactions and outline approaches for predicting CO yields. It is likely that similar detailed studies will be required in order to estimate yields for other toxic species such as HCN³⁷ that can be generated in fires.

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