An Algorithm for Estimating Carbon Monoxide Formation in Enclosure Fires

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ABSTRACT

This paper introduces an engineering approach for estimating the generation rate of carbon monoxide (CO) within a room containing a fire. Four CO formation mechanisms--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 a high-temperature, vitiated environment, and 4) approach to full-equilibrium combustion product concentrations in a rich, high-temperature upper layer--identified in recent experimental and modeling investigations are incorporated into a step-by-step algorithm. The understanding required to implement the algorithm in fire models is briefly discussed.

KEYWORDS: carbon monoxide, carbon monoxide production, enclosure fires, fire models, fire research, global equivalence ratio, room fires

INTRODUCTION

There is a need for models to estimate the amount of carbon monoxide (CO) generated by enclosure fires since at least two thirds of all deaths resulting from such fires in the United States can be attributed to smoke inhalation [1],[2] with the vast majority of victims located remote from the fire. CO is known to be the dominant toxicant in smoke. [3] A recent analysis suggests that even while the annual number of fire deaths is declining, the fraction due to carbon monoxide asphyxiation is increasing. [4] Here we present an engineering algorithm for predicting CO formation in enclosure fires. It is intended to be the first step in the development of effective models for this complex process.

The basis for the algorithm is a number of investigations carried out over the past few years. The focus is on the scenario of an intense fire within a room which is flashed over [5] and generally burning

underventilated. It is known that this scenario is responsible for most fire deaths. [3] In the following sections current approaches for estimating the amount of CO formed in such fires are discussed, findings from a number of studies are summarized, the experimental and analytical results are used as the basis for the development of an algorithm to estimate CO formation within the room of fire origin, the feasibility of implementing the algorithm is discussed, and a summary is provided.

CURRENT APPROACHES FOR CO ESTIMATION

Three basic approaches have been used for modeling the generation of CO during enclosure fires. Tsuchiya discusses the choices made for a number of fire models. [6] The first approach is that the user simply specifies the grams of CO generated per gram of fuel consumed. After reviewing a number of full-scale tests, Mulholland [7],[8] suggested a second approach, which is referred to as the "zeroth-order approximation", which recommends that production rates of 0.002 g CO/g fuel consumed for fully ventilated fires and 0.3 g CO/g fuel consumed for underventilated fires be used. The third approach recommends using values derived from experiments. [3],[9],[10] Two types of studies have been suggested as sources for the required values. The first is based on experiments in which flame gases are quenched in a hood placed above fires burning in an open laboratory. [11],[12],[13],[14] These experiments have shown that concentrations of gases trapped by the hood above a fire are correlated with the global equivalence ratio, ϕ_g, defined as the mass ratio of gases in the layer derived from fuel and from air normalized by the mass ratio of fuel and air required for stoichiometric burning. The existence of these correlations has been termed the global equivalence ratio (GER) concept. The correlations are fuel dependent, but have been obtained for a number of different fuel types. The second type utilizes measured CO/CO_2 ratios observed in actual enclosure fires to estimate CO production rates. [10]

SUMMARY OF EXPERIMENTAL FINDINGS

Most of the relevant research concerning CO formation in fires has been summarized in a NIST Monograph [15] and a subsequent review article [16]. Reviews of the studies which form the basis of the GER concept are included in these documents. Figure 1 reproduces results from the work of Morehart et al. [17] which shows how the observed mass fraction of CO in the gases trapped in a hood above a natural gas-fueled fire correlates with the GER. Earlier data from Toner et al. [18] is also included on the plot. Differences between the two sets of measurements have been attributed to the higher temperatures observed in the hood for Toner's experiments. [17] These results indicate that the GER concept is quite robust. Studies by Beyler show that the GER concept is applicable to a wide range of fuels, even though the correlations do change with fuel type. [11],[12] The results of Morehart et al. indicate that there is a weak dependence of the correlations on the upper-layer temperature, but that the correlations seem to achieve asymptotic behaviors for temperatures characteristic of upper layers in actual enclosure fires. Pitts has used detailed chemical kinetic modeling to show that a temperature effect should exist, but that once all oxygen is removed from the upper layer by reaction, the gases should become effectively nonreactive until very high temperatures (on the order of 1400 K) are attained. [19],[20] A recent modeling investigation by Gottuk et al. reached similar conclusions. [21]

Gottuk et al. at Virginia Polytechnic Institute and State University (VPISU) have investigated the composition of combustion gases generated in an enclosure designed to burn in a configuration

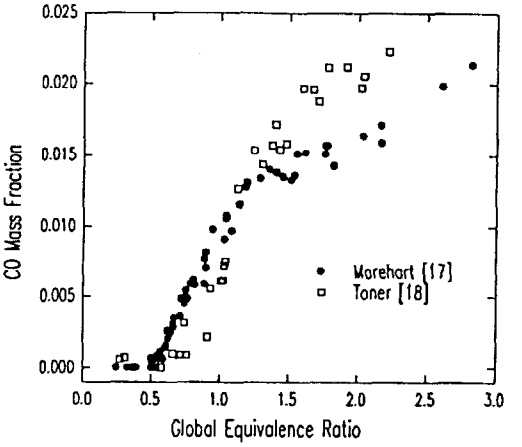

FIGURE 1. Carbon monoxide mass fractions measured in natural gas-fueled hood experiments are shown as a function of the GER. Figure generated from data in Morehart et al. [17] and Toner et al. [18]

similar to that of the hood experiments. [22] This enclosure had separate vents for air inflow and combustion gas exhaust which ensured that the fire plume in the lower layer had equal access to air from all directions and that there was insignificant direct mixing of the lower-layer air and upper-layer combustion gases. The results of this study indicate that the GER concept provides good predictions for concentrations of combustion gases, including CO, when the temperature effect is taken into account.

Bryner et al. [23],[24] studied CO formation in a reduced-scale enclosure (RSE, 2/5-scale model of standard ISO/ASTM room [25],[26]) with a single doorway. The fire was fueled by a single natural gas burner centered in the room. Upper-layer concentrations of CO, O_2, and CO_2 as well as vertical temperature profiles were measured for locations in the front and rear of the RSE.

The results for the RSE showed that very low concentrations of CO were generated when the fire was overventilated, i.e., $\phi_g < 1$, but that the concentrations of CO increased rapidly once ϕ_g became greater than one. Figure 2 shows results for time-averaged measurements of CO concentration in the front (i.e., close to the door) and rear of the upper layer. Concentrations of combustion gases observed in the rear of the enclosure were very similar to those reported by Toner et al. [18] in hood experiments using natural gas as fuel. For large ϕ_g, the concentrations of CO were roughly 2%. Unfortunately, concentrations in the front of the layer ($\approx$ 3%) can be seen to be roughly 50% higher than predicted by the GER concept. Strong temperature nonuniformities were also observed in the RSE upper layer, with higher temperatures measured in the front than in the rear.

The degree of nonuniformity observed in the temperature and concentration fields of the upper layer in the RSE for underventilated burning was surprising. Analysis of all of the available data indicated that the observations were the result of air entering and rapidly mixing into the front of the upper layer directly from the lower layer instead of being entrained into the fire plume [15],[16],[23],[24]. Evidence for this conclusion included measurements of lower local equivalence ratios in the front than in the rear of the upper layer and a preliminary field modeling investigation

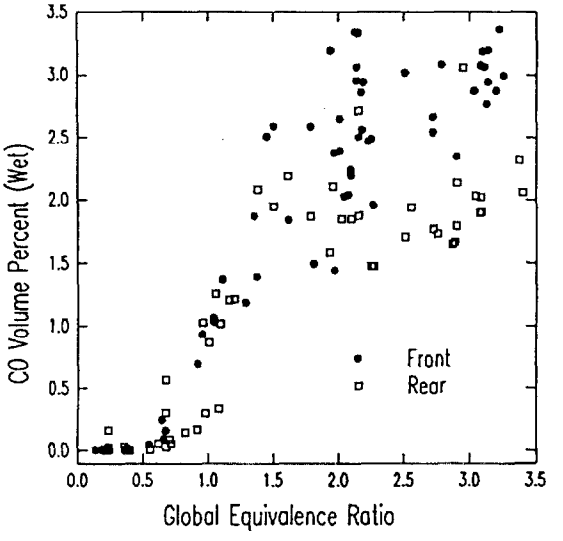

FIGURE 2. Measured CO concentrations in the front and rear of the upper layer during pseudo-steady-state burning of natural gas in the RSE are shown as a function of the global equivalence ratio. [23]

which indicated that very lean lower-layer gases were deposited in the front of the enclosure by direct mixing into the upper layer. [27] The direct entrainment into an upper layer is not believed to occur in the hood or the VPISU enclosure fire experiments due to their symmetric configurations. Air entrained directly into a fuel-rich upper layer is expected to react with excess fuel to produce CO in preference to CO_2, thus explaining the higher CO concentrations observed in the front of the upper layer. [15],[16],[19],[20] The heat release as a result of the additional reaction provides a partial explanation for the higher temperatures observed in the front of the RSE.

The direct entrainment and mixing of air into a rich, high-temperature upper layer of an enclosure fire is a mechanism for CO formation which is not included in the GER concept. The rich combustion gases created in a hood experiment are only the result of the quenching of reaction when a combusting buoyant plume enters a vitiated upper layer. It is therefore to be expected that when direct entrainment of air into the upper layer occurs, the GER concept will fail to predict upper-layer CO concentrations.

Much higher concentrations of CO than predicted by the GER concept have been observed in many fires involving wood as fuel. A good example is the study of Levine and Nelson, who experimentally reconstructed a fire in Sharon, PA where CO was implicated in several fire deaths. [28] This fire took place in an area with a very heavy fuel loading of wood. During the fire simulation, CO concentrations as high as 8% were observed. This value should be contrasted with a value of roughly 3% which was observed in the hood experiment of Beyler [12] using wood as fuel, as well as wood-fueled enclosure experiments at VPISU designed to mimic the hood experiments. [22] This is another type of fire where the GER concept fails to predict the observed CO production.

Pitts et al. hypothesized that the high concentrations of CO observed in the Sharon fire test resulted from the direct formation of CO by wood undergoing high-temperature pyrolysis in a highly vitiated

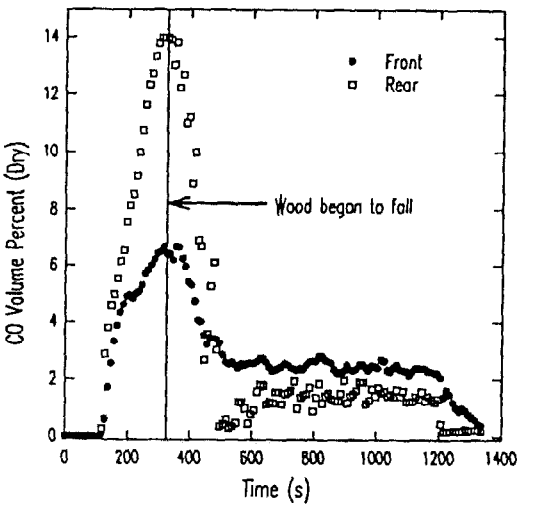

FIGURE 3. Volume concentrations of CO observed in the front and rear of the upper layer during a 400 kW natural gas fire in the RSE with its ceiling and upper walls lined with plywood. [29]

environment. [15],[16],[29] In order to test this hypothesis, a series of experiments were performed in the RSE for which the ceiling and upper walls (down to 36 cm from the ceiling) were lined with 6.3-mm-thick plywood. Natural gas fires having various heat-release rates (HRRs) were then burned and concentrations of CO and other combustion gases were monitored in the upper layer. Figure 3 shows an example of the CO mole fraction behavior as a function of time for the wood-lined RSE in which a nominal 400 kW natural gas fire was burned. For these experiments, the concentrations of CO increased rapidly, reaching levels as high as 14% in the rear of the upper layer and 6% in the front. These results provide direct evidence that pyrolysis of wood in a high temperature, anaerobic environment does generate significant concentrations of CO.

By using measured HRRs for the fires and an estimate for the heat release per gram of wood pyrolyzed, it was possible to estimate the mass-loss rate of the pyrolyzed wood per unit area of exposed surface. The mass-loss rate increased monotonically with time during the fire and reached a maximum on the order of 10 $gs^{-1}m^{-2}$ just before the wood collapsed and fell from the ceiling. Temperature measurements in the enclosure demonstrated that the overall pyrolysis process is endothermic.

The wood-lined-RSE results demonstrate that a third mechanism for CO formation in enclosure fires exists. The GER concept alone will not be able to make accurate predictions of CO formation when significant anaerobic pyrolysis of wood or other cellulosic material is occurring.

Much of the discussion thus far is based on measurements recorded in reduced-scale enclosures. In order to test whether or not these findings are valid for real-scale fires, a series of fires was burned at NIST in a standard size room having dimensions of 2.44 × 2.44 × 3.05 m (referred to as the full-scale enclosure (FSE)). A natural gas burner was again used as the fuel source. The following discussion is based on preliminary analysis of these burns performed in the late spring of 1994. [30]

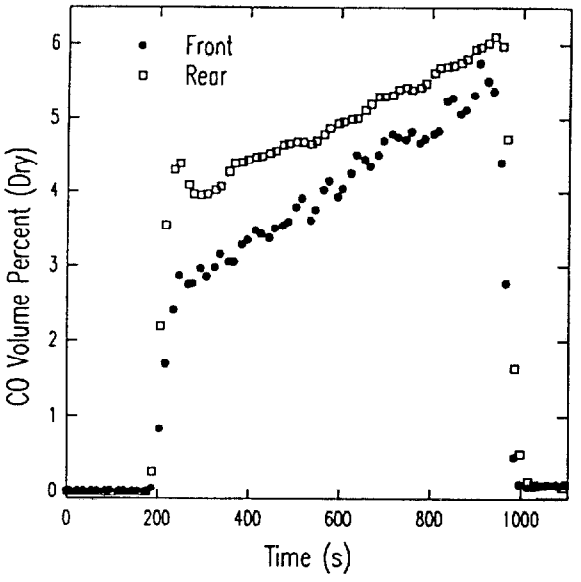

FIGURE 4. CO concentrations observed as a function of time in the front and rear of the upper layer during a nominal 3.2 MW natural gas fire in the FSE [30].

The experimental results indicate that the FSE fires became underventilated for natural gas fires larger than a nominal HRR of roughly 1.5 MW. This value is in good agreement with a prediction based on the corresponding value for the RSE and the expected flow variation through the doorways for the two enclosures. [31] Smaller HRR fires (i.e., 500 and 900 kW) should be fully ventilated. Measured upper-layer gas concentrations were consistent with this expectation. Significant O_2 concentrations were observed, CO_2 concentrations were relatively low, and CO concentrations were very close to zero.

Fires having HRRs corresponding to $\phi_g \approx 1$ (i.e., 1.1 and 1.3 MW) yielded results which were similar to those observed in the RSE. CO_2 concentrations in the rear of the upper layer were on the order of 10% to 12% while values of 8.0% to 10.0% were observed in the front. These values suggest that the gases in the rear of the enclosure have a local equivalence ratio (ϕ_l) which is close to 1 while those in the front are somewhat lower. CO concentrations behaved in a manner consistent with this conclusion. In the rear of the enclosure values of 1.5%-2.5% were observed, and values in the front were close to zero as expected for fully ventilated burning. O_2 concentrations of 2% to 3% were observed in the front of the enclosure, while values in the rear were very close to zero. These results demonstrate clearly that values of ϕ_l are significantly lower in the front of the enclosure than in the rear. A similar conclusion was reached for the RSE [15],[16],[23],[24], but the experimentally observed differences were not as well defined as for the full-scale tests.

CO concentrations observed for fires having HRRs sufficient to ensure underventilated burning with $\phi_g > 1.5$ were very different than observed in the RSE as can be seen in Fig. 4. Immediately following the start of the fire, CO concentrations increased to roughly 3% and 4% in the front and rear of the upper layer. For the remainder of the fire period the CO concentrations continued to increase, approaching values of 5%-6% for the two locations by the end of the burn. These CO

concentrations are much higher than observed in the RSE, and the relative magnitudes between the front and rear locations for the FSE are reversed while the relative differences are smaller.

For both enclosures, upper-layer temperatures were observed to increase with time. However, higher upper-layer temperatures were attained in the FSE tests than in the RSE for comparable ϕ_g. This can be understood by recognizing that the wall-surface-area to volume ratio of the RSE is greater than for the FSE, and a larger fraction of the released heat should be lost to the walls for the smaller enclosure. Additionally, the scaling of the doorways for the two enclosures is such that a larger fraction of the energy in the upper layer can be radiated from the smaller enclosure. Both effects should lead to a higher fraction of the energy being trapped in the upper layer of the FSE, and hence higher temperatures for scaled HRRs.

Due to upper-layer temperatures at certain locations exceeding the limit for the chromel/alumel thermocouples used, the maximum temperatures in the upper layer of the FSE are uncertain. Limited measurements with platinum/platinum-rhodium thermocouples indicated that upper-layer temperatures in the front of the FSE for fires with $\phi_g > 1$ approached 1400-1500 K.

The growth of CO concentrations in the upper layer with time in the FSE seems to be associated with increasing upper-layer temperatures. The time behaviors are similar. Significantly, Pitts has shown that mixtures of combustion gases which are kinetically frozen at lower temperatures begin to react and approach thermodynamic equilibrium concentrations at temperatures on the order of those observed in the FSE. [20] In this temperature range the formation of CO is strongly favored, and equilibrium concentrations of CO approach 16% for $\phi_g = 3$. Therefore, the most plausible explanation for the high CO concentrations observed in these experiments is that the upper-layer temperature has increased to the point where the rich combustion-gas mixture begins to react and approach equilibrium. The ultimate CO concentrations attained will be a function of residence time and reaction rate.

The approach of a nonequilibrium gas mixture towards thermodynamic equilibrium represents still another mechanism for CO formation in enclosure fires and, when it occurs, can lead to much higher concentrations of CO than predicted by the GER concept.

A single experiment was conducted in which the ceiling and upper walls down to 76 cm from the ceiling of the FSE were lined with 12.7-mm-thick plywood. A 2.0 MW natural gas fire was used. Enhanced CO concentrations (8% in the front of the room and 12% in the rear) which were very similar to those measured in the RSE were observed. Temperature levels were significantly suppressed from those for underventilated fires in the absence of wood. The formation of CO by anaerobic pyrolysis of wood does not seem to depend on enclosure size.

To summarize, there are at least four mechanisms for CO formation in enclosure fires. These are:

1) **Quenching of a turbulent fire plume upon entering a rich upper layer.** This is the mechanism considered by the hood experiments and the GER concept.
2) **Mixing of oxygen directly into a rich, high-temperature upper layer with subsequent reaction.**
3) **Pyrolysis of wood in high-temperature, vitiated environments.**

4) **Approach to full-equilibrium combustion product concentrations in a rich, high-temperature upper layer.**

It is important to note that the only mechanism which is captured by the GER concept is the first. It is particularly disconcerting that each of the other mechanisms results in the formation of additional CO. On this basis, it can be concluded that the GER concept provides an estimate for the least amount of CO which is likely to be generated by an enclosure fire. More reliable estimates must consider the additional formation mechanisms.

ENGINEERING ALGORITHM FOR PREDICTING CO FORMATION IN ENCLOSURE FIRES

The findings of the experimental and analytical studies discussed above have provided insights into the physical and chemical mechanisms responsible for CO formation during enclosure fires. These findings have been used to construct the engineering algorithm or decision tree shown in Fig. 5 for estimating CO production rates. By systematically following the decision tree, it should be possible to identify which CO formation mechanisms are important for estimating the amount of CO generated for a given enclosure fire, and, provided sufficient knowledge of the various controlling parameters is available, develop meaningful estimates for the amount of CO generated.

In order to use this algorithm it will be necessary to make estimates for a number of fire properties. Some of the parameters which may need to be specified include:

1) Values of ϕ_g for the enclosure as a function of time.
2) Species yields for a fire plume quenched by an upper layer as a function of ϕ_g.
3) Temperature as a function of time for the upper layer.
4) Amount of air entering the upper layer by direct entrainment as a function of time.
5) The surface area of any wood located in anaerobic regions of the room.
6) Estimates for the pyrolysis rate of wood as a function of temperature and time when subjected to nonreactive gases or intense flame radiation.
7) Estimates for the mass of CO generated per mass of wood pyrolyzed under anaerobic conditions.
8) Estimates for equilibrium concentrations of upper-layer gases, conversion rates for nonequilibrium gas mixtures towards thermodynamic equilibrium as a function of temperature, and combustion gas residence times within the enclosure.

FEASIBILITY OF IMPLEMENTING THE ALGORITHM

It is beyond the scope of this paper to try and speculate how each of these fire properties may be specified, but a few general comments are warranted. Since an underventilated, flashed-over enclosure fire is the scenario responsible for the vast majority of smoke inhalation fire deaths in the U.S., it is this scenario which should be the focus for predicting CO. It is worthwhile to note that it is likely that very good estimates of CO production rates for overventilated enclosure fires should be obtainable from yields measured for fires burning in the open. [6],[32]

The following comments pertain to underventilated fires. The investigations which form the basis of the GER concept indicate that the generation rates of combustion species by the quenching of a fire plume upon entering a rich upper layer are unique functions of the GER. While there is a

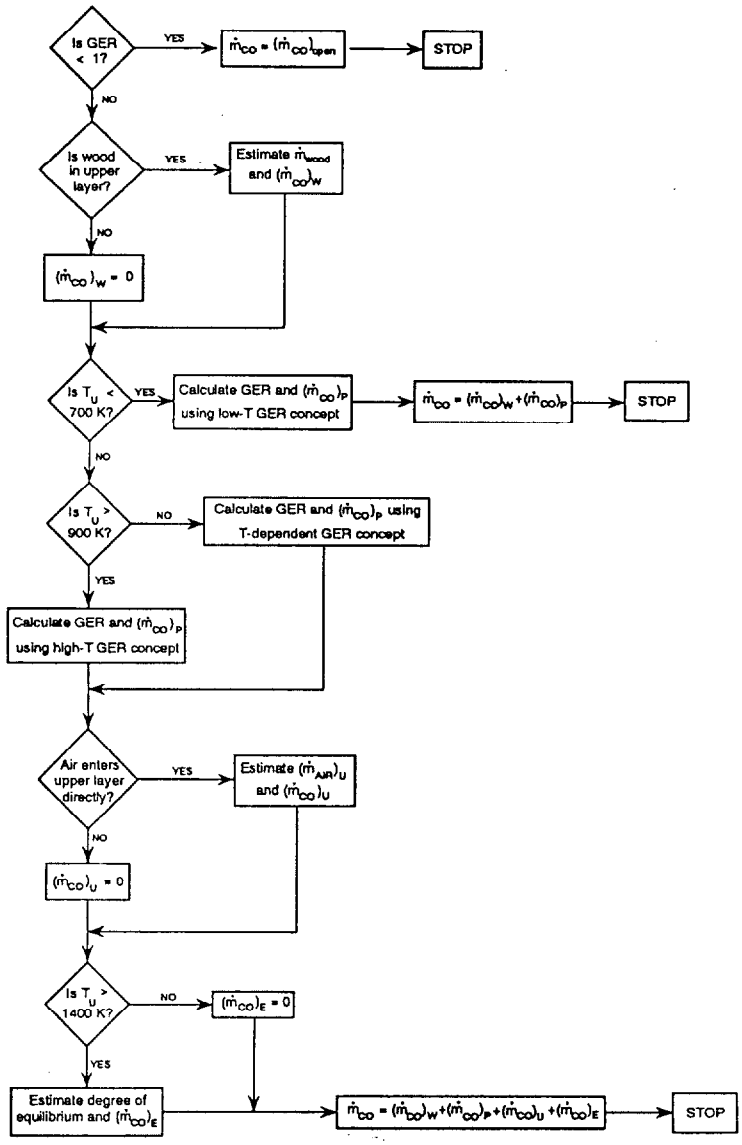

FIGURE 5. An algorithm to predict the generation of carbon monoxide during enclosure fires is shown. Symbols are defined as follows: GER is the global equivalence ratio, T_u is the upper-layer temperature, $\dot{m}$ are mass generation or entrainment rates with subscripts representing carbon monoxide (CO) formation, pyrolysis products of wood decomposition (wood), and air mixing into an upper layer of a fire (AIR). Subscripts associated with CO mass generation rates refer to CO formation by fires burning in an open environment (open), by wood pyrolysis in anaerobic environments (W), by quenching of a turbulent fire plume upon entering a rich upper-layer above a fire (P), by mixing air directly into a rich high temperature upper layer of a fire with subsequent reaction to generate CO (U), and by the upper layer of a fire becoming hot enough for the rich gases to begin to approach thermodynamic equilibrium (E).

temperature effect, it should be possible to estimate or measure correlations for a variety of fuels over the appropriate temperature range. Experiments suggest that it should be possible to estimate the mass-loss rate of wood or other cellulosic material in hot, anaerobic regions of an upper layer from direct measurements or by inference from heat-release-rate behavior. It should also be feasible to estimate the CO yield from this pyrolysis even though, to our knowledge, such measurements have not been reported previously for the conditions typical of flashed-over upper layers in enclosure fires.

Most measurements of fire gases in upper layers indicate that the mixtures are "kinetically frozen" and that combustion products do not approach thermodynamic equilibrium during normal residence times. Detailed chemical kinetic modeling supports this conclusion. [19]-[21] While it remains to be shown, it is the likely that upper-layer combustion gas concentrations can be specified sufficiently to allow detailed chemical kinetic modeling estimates for the rate at which upper layer gases approach thermodynamic equilibrium.

The parameter which is likely to be the most difficult to estimate is the amount of air mixed directly into the upper layer as opposed to entering by way of the fire plume. The studies discussed above indicate that such mixing does occur and that it can result in the formation of significant CO. However, the author is unaware of any previous investigations which can be used to provide reliable engineering estimates for the amount of air entering an upper layer directly. It is easy to speculate that such entrainment is likely to be strongly dependent on enclosure configuration and fuel distribution. The detailed kinetic modeling studies provide clear evidence that for rich upper layers, any organic fuel which reacts with air mixing rapidly into the layer will generate CO in preference to CO_2. Further investigations are required before reasonable estimates of the amount of CO formed in this way can be made.

FINAL COMMENTS

This paper presents an algorithm for CO formation in enclosure fires which is appropriate for use in fire models. The extensive experimental and modeling studies which form the foundation for the algorithm are summarized, and appropriate references are provided. It is clear that much additional work must be done before predictions of CO formation can be made with confidence. However, the algorithm should allow much improved predictions as compared to existing approaches which generally underpredict the amount of CO formed in the underventilated enclosure fires primarily responsible for fire deaths.

The work described here is aimed at developing a predictive capability for CO formation within flashed-over, underventilated enclosure fires. It provides no guidance as to the fate of such CO once it exits the enclosure. Under some conditions, the CO will burn out and high concentrations will not be transported large distances from the burn room. In other cases the potentially reactive flame gases exiting the enclosure are likely to be quenched with the result that high concentrations of CO generated within the room may be transported to remote locations where there are potential victims. An ongoing investigation is aimed at identifying the conditions necessary for CO to be transported. [33]

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