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CARBON MONOXIDE FORMATION ALGORITHM

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ABSTRACT

This paper discusses an engineering approach for estimating the generation rate of carbon monoxide (CO) within a room containing a fire. The algorithm incorporates four CO formation mechanisms which have been identified in past investigations.

1. INTRODUCTION

At the present time there is no generally accepted model for the formation of carbon monoxide (CO) by enclosure fires. The need for such a model is crucial since roughly two thirds of all deaths resulting from such fires can be attributed to smoke inhalation [1],[2]. CO is the dominant toxicant in smoke [3]. 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 experimental basis for the algorithm is a long-term effort in BFRL--the Carbon Monoxide Production and Prediction Priority Project--which has been ongoing for six years. The research plan under which this research has been performed is available [4].

The research has focused on the scenario of an intense fire within a room which is flashed over [5]. It has been shown that this scenario is responsible for the vast majority of fire deaths [3]. The algorithm which is presented is intended for this type of fire. In the following sections current approaches for CO estimation are discussed (2), experimental findings from a number of studies are summarized (3), the experimental findings are used as the basis of an algorithm for estimating CO formation within the room of fire origin (4), and a summary is provided (5).

2. CURRENT APPROACHES FOR CO ESTIMATION

Three basic approaches have been used in BFRL for modeling the generation of CO during enclosure fires. The first is that the user simply specifies the grams of CO generated per gram of fuel consumed. After reviewing a number of full-scale tests, George Mulholland 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 [6],[7]. The third approach [3] recommends using values derived from experiments in which flame gases are quenched in a hood located above a fire burning in an open laboratory [8],[9],[10],[11]. These experiments have shown that concentrations of gases in the upper layer are correlated with the global equivalence ratio, ϕ_g , which is 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.

3. SUMMARY OF EXPERIMENTAL FINDINGS

Most of the relevant research concerning CO formation in fires has been summarized in a NIST Monograph [12] and a subsequent review article [13]. Review of the studies which form the basis of the GER concept are included in these documents. It is shown that the GER concept is quite robust and applicable to a wide range of fuels. A slight dependence of the correlations on upper-layer temperature has been identified, but the correlations seem to achieve asymptotic values 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 be effectively nonreactive until very high temperatures are reached [14],[15].

Gottuk et al. at Virginia Polytechnic Institute and State University have investigated the combustion gases generated in an enclosure fire designed to burn in a configuration similar to the hood experiments [16]. 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 the lower-layer air and combustion gases did not directly mix significantly. The results of this study indicated that the GER concept provided good predictions for concentrations of combustion gases, including CO, when the temperature effect was taken into account.

Bryner et al. studied CO formation in a reduced-scale enclosure (RSE, 2/5-scale model of a standard ISO/ASTM room [17],[18]) containing a single doorway [12],[13],[19],[20]. The fire was formed by a single natural gas burner centered in the room. Upper-layer concentrations of CO, O₂, and CO₂ 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. Concentrations of combustion gases observed in the rear of the enclosure were very similar to those reported by Toner [21] 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 ($\approx 3\%$) were observed to be roughly 50% higher than predicted by the GER concept. Strong temperature nonuniformities were also observed in the upper layer with higher temperatures measured in the front than 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 in the front of the upper layer directly from the lower layer instead of being entrained into the fire plume [12],[13],[19],[20]. Such direct entrainment into an upper layer is not believed to occur in the hood experiments or the VPISU enclosure fires. Air entrained directly into a rich upper layer is expected to react with excess fuel to produce CO in preference to CO₂, thus explaining the higher CO concentrations observed in the front of the upper layer [12]-[15]. The heat release as a result of the additional reaction provides a partial explanation for the higher temperatures observed in the front of the enclosure.

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 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 [22]. 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 [9] using wood as fuel, as well as the enclosure experiments at VPISU designed to mimic the hood experiments [16]. This is another case where the GER concept fails to predict observed CO concentrations.

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 environment [12],[23]. In order to test this hypothesis, a series of experiments were run in the RSE for which the ceiling and upper walls (36 cm from 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. 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⁻¹m⁻² just before the wood collapsed. Temperature measurements in the enclosure demonstrated that the overall pyrolysis process is endothermic.

The wood-lined-enclosure results demonstrate that a third mechanism for CO formation in enclosure fires, namely pyrolysis of wood in a high-temperature anaerobic environment,

exists. The GER concept alone will not be able to make accurate predictions of CO formation when significant anaerobic pyrolysis of wood is occurring.

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

The experimental results indicate that the full-scale fires became underventilated for a flow of natural gas corresponding to a 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 ventilation based on the known doorway sizes for the two enclosures.

Smaller HRR fires (i.e., 500 and 900 kW) should be fully ventilated. Measured upper-layer concentrations are consistent with this expectation. Significant oxygen concentrations were observed, carbon dioxide 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 somewhat different than observed in the RSE. CO₂ concentrations in the rear 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 the front is 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, while values in the front were close to zero as expected for fully ventilated burning. As would be expected, oxygen concentrations of 2%-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 [12],[13],[19],[20], but the experimental observations were not as well defined as in 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. Immediately following the start of the fire, CO concentrations increased to roughly 3% 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 6%-7% for both locations by the end of the burn period. CO concentrations in the full-scale enclosure reached much higher levels than observed in the RSE, and differences between the front and rear locations were much less obvious than observed for the RSE.

For both enclosures, upper-layer temperatures were observed to increase with time. However, higher upper-layer temperatures were observed in the full-scale 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 full-scale enclosure, 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 real-scale enclosure, and hence higher temperatures for scaled HRRs.

Due to the temperature maxima reached and the limits of the chromel/alumel thermocouples used, the maximum temperatures in the upper layer of the full-scale room are uncertain. Limited measurements with platinum/platinum-rhodium thermocouples indicated upper-layer temperatures in the front of the full-scale enclosure for fires with $\phi_g > 1$ approached 1400 K-1500 K.

The growth of CO concentrations in the upper layer with time in the real-scale facility seems to be associated with the increasing upper-layer temperatures. The time behaviors are similar. Furthermore, Pitts has shown that mixtures of combustion gases which are kinetically frozen at lower temperatures begin to react and approach thermodynamic equilibrium concentrations at higher temperatures [15]. 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 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 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 full-size enclosure 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, the research thus far has indicated that there are at least four potential 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.
- 2) **Mixing of oxygen directly into a rich, high-temperature upper layer.**
- 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 one. 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.

4. ENGINEERING ALGORITHM FOR PREDICTING CO FORMATION IN ENCLOSURE FIRES

The findings of the experimental and analytical studies discussed in the last section have been used to construct the engineering algorithm for CO production rates shown in Figure 1. In order to use this algorithm an engineer will need to be able to make engineering estimates for a number of fire behaviors. Some of the parameters which may need to be specified include:

- 1) Time behavior of ϕ_g for the enclosure as a function of time.
- 2) The correlations of species yields and/or concentrations for the upper layer as a function of ϕ_g .
- 3) Temperature as a function of time for the upper layer.
- 4) Amount of air directly entering the upper layer as a function of time.
- 5) The surface area of wood which is located in anaerobic regions of the room.
- 6) Estimate for the pyrolysis rate of wood as a function of temperature and time when subjected to nonreactive gases or intense flame radiation.
- 7) Estimate 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 equilibrium as a function of temperature, and combustion gas residence times within the enclosure.

6. Summary

This report has provided a summary and references for an extensive research program designed to characterize CO formation mechanisms within enclosure fires. The findings of these investigations have been used to develop an engineering algorithm for the prediction of CO formation during enclosure fires for use in fire models.

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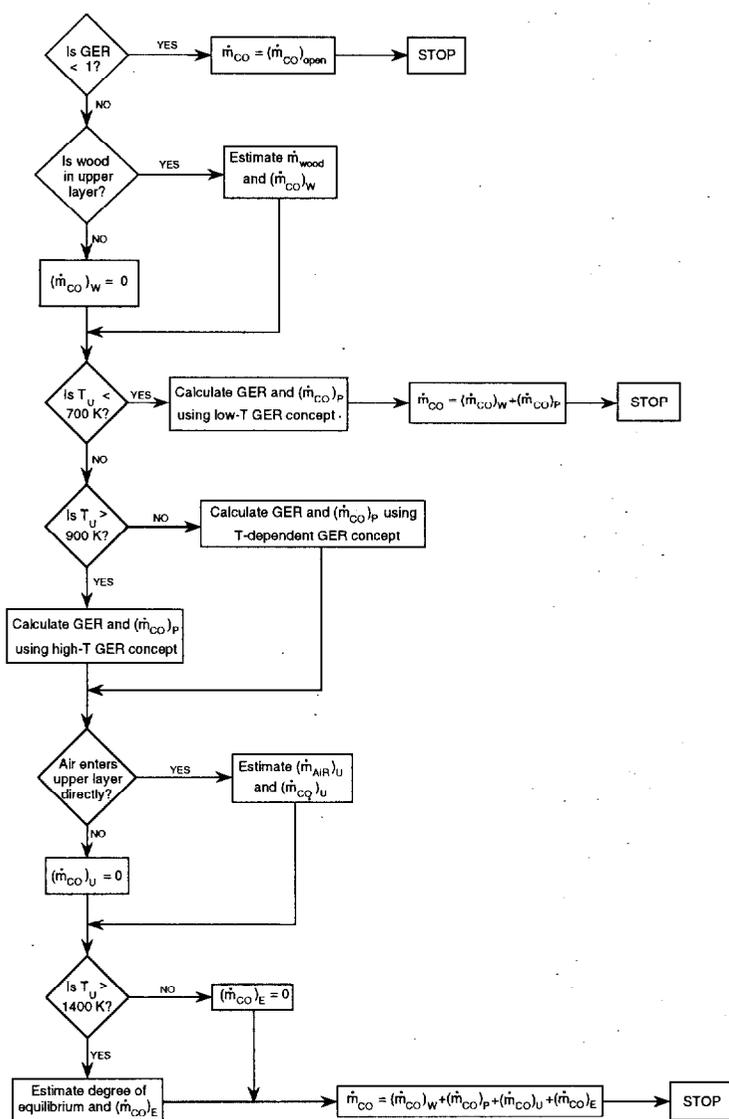


Figure 1. An algorithm for predicting the generation of carbon monoxide during enclosure fires is shown. The symbols are defined as follows: GER is the global equivalence ratio, T_u is the upper-layer temperature, \dot{m} are mass generation or entrainment rates with subscripts representing carbon monoxide (CO) formation, pyrolysis products of wood decomposition (wood), and air mixing into an upper layer of a fire (AIR). Subscripts associated with the 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).

Discussion

Question: Do you have flame shape data?

William Pitts: We do have data on several things. These include local equivalence ratio measurements, front and rear. We find experimentally that they are lower in the front. That means that more air by whatever path has reached the front as opposed to the rear. The second piece of evidence has to deal with some very simple modeling that we've done of these flow systems. What they indicate is exactly what I described, air going into the upper layer without passing through the flames. They suggested this air ultimately ends up in the front of the enclosure exactly where we see the higher concentrations of CO. These have not been done carefully, but I feel that they're indicative of what's happening. I think the evidence indicates that there is indeed this mechanism for air to indirectly to the upper level.

I did not mention temperature measurements today but we do, indeed, see 200-300 K higher in the front than in the rear. We attribute it to a combination of additional heat releases associated with the oxygen being entrained directly into the upper layer and to residence time effects. There are recirculation zones in the rear of the enclosure which makes the residence time much longer than for gases passing directly out of the front of the enclosure, so we think heat loss is contributing there as well.