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Application of Thermodynamic and Detailed Chemical Kinetic Modeling to Understanding Combustion Product Generation in Enclosure Fires

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ABSTRACT

Experiments in idealized two-layer fire environments have demonstrated that concentrations of carbon monoxide and other gaseous combustion products can be correlated in terms of the global equivalence ratio. In this paper the results of detailed chemical kinetic modeling and equilibrium calculations are used to gain insight into the chemical stability of the gases observed within the upper layers of such fires. It is demonstrated that the production of upper-layer gases is kinetically controlled and that for rich conditions concentrations of the upper-layer gas components are far from those expected for thermodynamic equilibrium at the layer temperatures. Criteria are provided for determining whether or not the correlations can be employed to predict the generation of combustion products in enclosure fires.

INTRODUCTION

Roughly two-thirds of all deaths resulting from enclosure fires can be attributed to the presence of carbon monoxide (CO)^{1,2} which is known to be the dominant toxicant in fire deaths.³ The mechanisms responsible for the generation of high concentrations of CO in fires are poorly understood. A long-term program at the Building and Fire Research Laboratory (BFRL) of the National Institute of Standards and Technology (NIST) is seeking to develop an understanding of and predictive capability for the generation of CO in fires.⁴

A major step in the understanding of CO formation in enclosure fires has been provided by a series of idealized experiments performed at Harvard University⁵⁻⁷ and the California Institute of Technology.⁸⁻¹³ Due to the configuration of the experiments they will be referred to as 'hood experiments'. The experimental findings and conclusions based on the hood experiments are summarized in the following section. The most important finding of these studies is: *major chemical species* (*including CO*) trapped in a hood located above a fire burning in an open laboratory can be correlated in terms of the global equivalence ratio (GER, defined as the mass ratio of gas in the hood derived from the fuel to that originating in air normalized by the fuel/air mass ratio required for stoichiometric burning). The existence of these correlations has been termed the 'global equivalence ratio concept'.

The configuration of the hood experiments was designed to be an idealization of the two-layer model¹⁴ often used to describe enclosure fires. If the GER concept could be applied to enclosure fires it would offer the possibility of predicting the production of major combustion species. In this paper results from detailed chemical-kinetic models of upper-layer reaction behavior and thermodynamic arguments are used to provide a partial answer to the question: is it appropriate to use the GER concept to predict species production by enclosure fires, and if so, under what conditions is its use appropriate? Additional implications of the kinetic and thermodynamic results for understanding the experimental findings of the hood experiments and the behavior of enclosure fires are also discussed.

HOOD EXPERIMENTS AND THE GLOBAL EQUIVALENCE RATIO CONCEPT

'Hood experiments' are so-named because of the experimental configuration used. In the experiments a hood was located above a fire burning in an open laboratory. Hot combustion gases were trapped by the hood, ultimately forming a well-defined upper layer which the fire plume entered. The vertical position of the fire source could be varied such that flames extended into the hood. For a sufficiently short burning distance between the burner and upper layer, underventilated burning conditions could be generated in which the flame was quenched upon entering the hood and products of incomplete combustion were formed and trapped in the hood. Experiments showed that the gases in the upper layer, away from the fire plume, were well mixed. By varying the burner of fuel size and the separation distance of the fire source from the base or the upper layer, it was possible to change systematically the mass ratio of combustion gases in the hood derived from fuel and from entrained air. Generally, the fires were allowed to burn long enough for the temperature and composition of the upper layer to attain steadystate behavior.

The simple configuration and steady-state nature of the hood experiment allows detailed measurements of species concentrations in the upper layer. From these measurements it is possible to derive the global equivalence ratio in the hood. By standard convention, the symbol ϕ denotes equivalence ratio. For the hood experiments it is possible to define several different ϕ s. Here we will consider two. The global equivalence ratio (ϕ_g) defined in the Introduction and the plume equivalence ratio (ϕ_g) defined as the fuel mass flow rate divided by the air mass entrainment rate into the plume below the upper layer normalized by the fuel/air mass ratio required for stoichiometric burning. Note that for steady-state cases where the flow conditions are such that both air and fuel enter the upper layer only by way of the fire plume, ϕ_p and ϕ_g are identical.

Beyler was the first to attempt to correlate his measurements of combustion gas concentrations in the upper layer with the GER.⁵⁻⁷ He studied a variety of solid, liquid and gaseous fuels. Values of ϕ_p were determined by measuring the total gas flow into the hood (by balancing extraction of a known amount of gas from the hood to give a constant layer height) and using the measured fuel flow rate and compositions of the upper layer. Since the experiments were done for steady-state conditions, to a very good approximation, ϕ_p was equal to ϕ_g . Beyler found an excellent correlation of major gas species with ϕ_g which was independent of fire size, upper-layer temperature (range of 470–800 K), and separation of the upper layer and fire base. By varying the fuel, Beyler demonstrated that the product concentrations were fuel dependent, but that data for a range of fuels supported the GER concept.

The major conclusions of Beyler's work can be summarized as:

- (1) Major flame species including CO can be correlated in terms of ϕ_{g} .
- (2) Relatively constant concentrations of CO are observed at low (<0.5) and high $(>1.3) \phi_g$.
- (3) The generation of CO under rich conditions is considerably greater than for fuel-lean conditions.
- (4) The concentrations of CO generated for rich conditions are fuel dependent, but can be correlated with fuel structure. Oxygencontaining fuels generate the highest CO levels while especially thermally stable fuels, such as toluene, generate the lowest. Hydrocarbon fuels fall in the middle.

The observed concentrations of products of incomplete combustion had interesting dependencies on ϕ_g . The concentration of CO was observed to begin to increase for $\phi_g > 0.5$, while the other products of incomplete combustion (hydrogen and total hydrocarbons) began to increase at slightly higher ϕ_g . For a ϕ_g of 1 there was roughly 2% O₂ remaining in the fire gases, and measurable amounts of O₂ were present at the highest ϕ_g (1.8) recorded. The coexistence of fuel and O₂ for both lean and rich ϕ_g suggests that additional reaction of the fire gases would be possible if upper-layer temperatures were increased. Observed upper-layer temperatures were less than 800 K.

Several different hood experiments have been performed at the California Institute of Technology.⁸⁻¹³ Here we focus on the investigations of Toner and Morehart.¹⁰⁻¹³ Toner used a gas chromatography system which allowed accurate concentration measurements of a large number of species in the upper layer.¹⁰ It was possible to record concentrations for a sufficient number of species so that by combining the measurements with appropriate conservation laws he was able to report all major species concentrations directly without making any assumptions concerning burning behavior. Natural gas was the fuel. Temperatures in the upper layer covered a range of 500–870 K.

Measurements were made for CH₄, O₂, CO₂, CO, and H₂. All of the species concentrations were found to be well correlated in terms of ϕ_g . The only product of incomplete combustion observed for $\phi_g < 1$ was CO. H₂ and CH₄ only appeared for $\phi_g > 1$. The CO mole fraction began to increase for $\phi_g > 0.5$, and was of the order of 1% for $\phi_g = 1$. CO concentrations appeared to level off to a mole fraction of 0.019 for $\phi_g > 1.5$. These observations are consistent with Beyler's findings. A major difference was that oxygen concentrations for $\phi_g > 1$ approached zero in Toner's work. Beyler's experiments had indicated that significant concentrations of O₂ remained for rich mixtures in the upper layer. Toner's work was the first indication that the correlations in terms of ϕ_g depend on an uncharacterized (at the time his work appeared) variable.

Morehart made additional measurements for natural gas fuel using a larger hood system than Toner.^{11–13} A series of tubes with holes was placed within and near the top of the hood such that additional gas could be injected directly into the upper layer at positions well removed from the fire plume.

The new hood allowed ϕ_p and ϕ_g to be varied independently while maintaining a steady-state condition in the upper layer. For instance, by adding air to the upper layer it was possible to force ϕ_g to be lower than ϕ_p . The experiment was designed to model the conditions expected in a developing room fire. In the early stages of such a fire there is sufficient oxygen available, and the upper layer which begins to form is fuel lean. As the fire grows, its oxygen (air) demands increase, and the fire plume entering the upper layer is richer than the combustion gases trapped above. Eventually the upper layer becomes rich enough (i.e. the oxygen concentration decreases sufficiently) to quench the fire plume in this layer, and concentrations of products of incomplete combustion build up. A pseudo-steady-state burning may be reached in which ϕ_p and ϕ_g are the same (the condition modeled by the earlier experiments). A dying fire is expected to go through a reverse process. As the fire size decreases less oxygen is required, and ϕ_p becomes less than ϕ_g . It would be possible to model this process in the hood experiments by adding fuel to the upper layer. Such measurements were not reported by Morehart.

Hood temperatures observed by Morehart were in the 500-600 K range. Due to the larger volume of the hood and differences in insulation, these temperatures are generally lower than observed in the earlier hood experiments. Measurements were made for CH₄, O₂, CO₂, CO, H_2 , C_2H_6 , and C_2H_2 .¹¹ As in the earlier work, it was found that the major steady-state species concentrations within the hood were well correlated when plotted as a function of ϕ_{e} . This was true for cases where no air entered the hood directly ($\phi_g = \phi_p$) as well as cases when air was added directly to the upper layer, thus lowering ϕ_g relative to $\phi_{\rm p}$. The remarkable conclusion reached was that the concentrations of combustion gases in an upper layer of a hood depend only on the value of ϕ_g (even when $\phi_g \neq \phi_p$) suggesting that the generation rates for the chemical species only depend on this variable. The importance of this observation is great because it suggests that steady-state measurements of this type could be used to predict instantaneous concentrations during a developing fire.

Unfortunately, Morehart's results also revealed a new uncertainty concerning the GER concept. His results showed that there were significant systematic differences between his measurements of the products of incomplete combustion and those of Toner.¹⁰ The differences between the two sets of data were varied and complex. Figure 1 compares the two sets of measurements for carbon monoxide as a function of ϕ_g . CO concentration started to rise at higher ϕ_g for the Toner data, and CO concentrations for $\phi_g > 1.3$ were higher in Toner's hood. Acetylene showed a roughly similar behavior in the two studies. Morehart found unburned CH₄ for $\phi_g > 0.5$ while it was only detected for $\phi_g > 1$ by Toner. In all cases the CH₄ concentration was lower in the Toner experiments. Finally, measurements of H₂ and C₂H₆ con-



Fig. 1. Mole fractions of CO observed in the steady-state experiments of Toner¹⁰ and Morehart¹¹ are plotted as a function of the global equivalence ratio (ϕ_g) .

centrations had similar behaviors in both cases, only beginning to appear in significant concentrations for $\phi_g > 1$.

The behaviors for CO₂ and O₂ were also different in the two studies. For lean conditions the amounts of CO₂ observed by Morehart and Toner were similar, but for $\phi_g > 1$ Toner found higher concentrations. Figure 2 compares the oxygen measurements for the two studies. Similar to the work of Beyler,⁵⁻⁷ Cetegen⁸ and Lim,⁹ Morehart found decreasing, but significant, concentrations of O₂ for $\phi_g > 1$, while, as noted above, Toner's measurements¹⁰ indicated very little oxygen was present for rich conditions. This last observation clearly suggests that the reaction behavior was different in the two experiments.

Morehart considered possible reasons for the differences between his measurements and those of Toner. Based on experimental tests where the upper-layer temperature was systematically varied, he concluded that the variations were real and were the result of differences in the layer temperatures between the two experiments. The higher temperatures observed in the Toner hood resulted in more complete oxidation for rich conditions.

Morehart also reported limited measurements using ethylene and propylene fuels. Concentration behaviors were similar for the three fuels, but the absolute concentrations were dependent on fuel in agreement with Beyler's conclusion.^{5–7}



Fig. 2. Mole fractions of O_2 observed in the steady-state experiments of Toner¹⁰ and Morehart¹¹ are plotted as a function of the global equivalence ratio (ϕ_g).

Beyler had also used propylene as a fuel.^{5,6} Morehart compared his results for this fuel directly with Beyler's. There were significant differences between the two sets of measurements, but the variations were similar to those observed when the Morehart¹¹ and Toner¹⁰ natural gas data were compared. For instance, Morehart observed higher oxygen concentrations for $\phi_g > 0.5$, and CO and H₂ concentration behaviors were similar in both comparisons even though CO was observed for $\phi_g > 0.5$ while H₂ did not start to increase until the upper layer became rich. The similarity of the variations for natural gas and propylene fires suggests that temperature differences are responsible in cases. Indeed, upper-layer temperatures in the Beyler both experiments⁵ were at least 200 K higher than in the larger hood of Morehart. The observation of such differences for two experiments in different laboratories greatly strengthens the conclusion of a temperature effect on correlations of combustion gas species as a function of ϕ_{g} .

The experimental findings discussed above demonstrate that the composition of upper layers in the hoods above simple fires are well correlated by plotting the concentrations in terms of ϕ_g . This is true even when ϕ_p is not the same as ϕ_g . The correlations are insensitive to fuel supply rate and the separation of the fuel source and the layer interface. However, the correlations are found to depend on the fuel and the upper-layer temperature.

Even though the data are limited, there does seem to be some consistency in the dependence of the GER correlations on temperature. For upper-layer temperatures lower than 500 K the correlations are independent of the upper-layer temperature. As the temperature is increased in the range 500–700 K, shifts in the composition of the products are observed. The data suggest that the changes in composition are the result of oxidation of additional fuel to produce CO, CO_2 and H_2O . Concentrations of H_2 seem to be relatively insensitive to the temperature effect.

The degree to which oxygen reacts appears to be well correlated with temperature. Concentrations of O_2 observed by Beyler for rich conditions were lower compared to Morehart's measurements as expected based on the higher temperatures present in the Beyler hood. The decrease in O_2 concentration extended down to $\phi_g = 0.5$ where the first products of incomplete combustion were observed. On the other hand, the Toner measurements [which had the highest upper-layer temperatures (maximum of 870 K)] showed that the layer was nearly depleted of oxygen for rich conditions.

The dependence of the upper-layer concentrations of CO and CO_2 on temperature is not as clear. At higher temperatures the concentrations of CO_2 increased at rich conditions for both Beyler's and Toner's data as compared to the lower temperature results of Morehart. Strangely, the CO measurements with rich conditions for Beyler and Morehart were in good agreement while Toner measured higher concentrations of CO for rich conditions. These observations suggest that shifts in the relative compositions of these partially oxidized species are to be expected with increasing temperature. A similar dependence on temperature is found for comparisons of CO concentrations under lean upper-layer conditions. The data of Beyler and Morehart are in good agreement while Toner's results indicate that much lower CO levels are present.

Note that while the discussion has focused on the effect of temperature on the upper-layer concentrations, other related parameters are likely to be important. For instance, since the modifications in concentration appear to vary slowly with temperature, it is possible that the average residence time in the upper layer may also be an important variable.

It should be noted that local concentration measurements for the principal stable species in laminar diffusion flames have been shown to correlate well with the local equivalence ratio for a variety of fuels.^{15,16} Beyler⁶ was aware of the existence of these findings when he correlated the species concentrations in his hood experiment with the global

equivalence ratio.⁶ Beyler also pointed out that the observed correlations in the laminar flames and upper layers were quite different. As an example, maximum concentrations of CO observed in a laminar methane/air flame¹⁷ were at least a factor of two higher than those found in the natural gas hood experiments.¹¹ Other products of combustion show similar differences.

CALCULATIONAL APPROACHES

Detailed chemical-kinetic modeling of expected upper-layer reaction behavior

Morehart tried to address the temperature effect by performing detailed chemical-kinetic calculations of a plug-flow reactor for a rich mixture typical of his upper layer.¹¹ The calculations showed that such mixtures did become reactive for temperatures greater than 700 K in agreement with his experimental findings, but that the calculated changes in upper-layer composition were not consistent with the differences between the Toner and Morehart experiments.

Pitts has reported similar calculations using the experimental concentrations of combustion gases observed by Morehart as the starting point.¹⁸ Calculations were performed over a range of temperatures (700-1300 K), ϕ_g (0.5-2.83), and residence times (0-20 s). Effects of mixing behavior and heat loss variation were investigated by considering possible extremes: infinitely fast (perfectly stirred reactor model) and infinitely slow (plug-flow reactor) mixing models and by considering conditions for which the reactor temperature was held constant by allowing heat transfer to or from the reactor surroundings (isothermal case) and for which no heat transfer to or from the reactor took place (adiabatic case). The detailed chemical-kinetic calculations discussed in this paper were performed in the same way as described earlier.¹⁸ Briefly, codes provided by the Combustion Research Facility of the Sandia National Laboratory were used. A series of Fortran-based subroutines known collectively as CHEMKIN form the basis of the calculations.¹⁹ Sandia also provided 'drivers' to allow detailed chemical modeling for a plug-flow reactor (SENKIN)²⁰ and a perfectly stirred reactor (PSR).²¹

Following a careful literature search, a detailed mechanism for ethylene oxidation developed by Dagaut *et al.*²² was chosen for use in

the models. This mechanism consists of 31 molecular species undergoing 183 reactions. This mechanism has been validated with experimental data for temperature ranges and equivalence ratios similar to those of interest here.²² When available, the necessary thermodynamic data for the calculations were taken from a Sandia compilation.²³ Values for those species not available from this source were taken from Senkan.²⁴

Gottuk has performed similar modeling calculations in an attempt to understand the generation of combustion gases in a reduced-scale enclosure.²⁵ The findings of his investigation were consistent with the NIST calculations.¹⁸

Thermodynamic predictions of upper-layer composition

Several of the researchers at the California Institute of Technology attempted to use thermodynamic approaches to predict observed dependencies of flame gas concentrations on ϕ_g .⁹⁻¹¹ Equilibrium concentrations for major species were calculated as functions of ϕ_g assuming various upper-layer temperatures. The hypothesis was that the upper-layer gas composition might result from 'freezing' of the chemical reactions within the fire plume under conditions such that the gases were in full thermodynamic equilibrium. The calculations showed that no unique temperature existed which predicted the observed concentration variations with ϕ_g for all combustion species.

Related work has been published by Nakaya.²⁶ This author assumed that the upper-layer gases in an enclosure fire were at high enough temperatures to come into full chemical equilibrium before exiting the enclosure. An average temperature of 1200 K was assumed for the layer temperature. Predictions of combustion product composition were developed based on the hypothesis of full chemical equilibrium. By comparison with experimental data, it was concluded that the accuracy of the approach was good and that the analysis provided a useful means to predict toxic hazard.

During the course of the current work equilibrium compositions have been calculated using the subroutine DSTANEQ supplied by the Combustion Research Facility of the Sandia National Laboratories. With minor changes this code is the same as the original STANJAN code of Reynolds.²⁷ Possible components for the equilibrium mixture were assumed to be the same 31 molecular species used in the detailed chemical-kinetic calculations. Initial conditions were taken as room temperature mixtures of the combustion products observed by Morehart.¹¹

It should be noted that soot has not been included as a potential

combustion product in either the detailed kinetic or thermodynamic calculations. Insufficient information is available to treat the formation and destruction kinetics of soot in the environments of interest to this investigation. It is well known that if soot is added to the reaction products for the thermodynamic calculations, that all of the available carbon is converted to solid carbon (e.g. see Bilger¹⁵). Soot concentrations in natural gas fires are expected to be low and assuming no soot is present should be a good approximation for the current calculations. Such an approach may be inappropriate for other fuels which soot more strongly.

RESULTS

Detailed chemical-kinetic modeling

A discussion of the results for the detailed chemical-kinetic calculations can be found in Pitts.¹⁸ The results of this earlier investigation are summarized below and some additional details not provided in the earlier report due to space limitations are presented.

The major findings of the numerical study are:

- (1) Upper-layer gases are unreactive for temperatures less than 700 K.
- (2) Upper-layer combustion gases become reactive for temperatures greater than 800 K.
- (3) Reaction rates increase with temperature. For the lowest temperatures, residence times of 10 s of seconds were required for complete reaction, while periods of less than 1 s were required at 1300 K.
- (4) The products generated varied for lean and rich conditions and with temperature. For lean conditions products of complete combustion (i.e. water and carbon dioxide) were produced. For rich conditions, CO was produced in preference to CO_2 . At lower temperatures (<1100 K) water was generated in preference to hydrogen, but for temperatures greater than 1100 K hydrogen was the major product. Since hydrogen does not require an oxygen atom, more oxygen was available for oxidation of fuel and higher concentrations of CO were formed at the higher temperatures.
- (5) The reaction behavior was not strongly affected by the mixing

conditions. Examples of calculations demonstrating this point are shown below.

(6) For adiabatic conditions, reaction for short residence times resulted in increases in temperature. In some cases the effects of the temperature increases on the amounts of final products were small for the same initial temperature. In other cases, the changes in the final product distributions for the two heat loss conditions were quite dramatic. Examples of calculated results and an explanation for the observed behaviors are provided below.

As explained in Ref. 18 the generation of CO in preference to CO_2 can be understood in terms of the relative reactivity of the important free radicals (i.e. OH_{\cdot} , and HO_2) with CO (to form CO_2) and unburned fuel (forming CO through a series of rapid reactions). The reactions of these radicals as well as H atoms with fuel are much faster than with CO. As a result, radical concentrations are suppressed and the fuel is only partially oxidized to CO. This condition holds as long as any significant concentration of fuel remains in the reacting mixture. This fuel inhibition effect was demonstrated dramatically by calculations for ϕ_g which were slightly rich.¹⁸ Initially the fuel was oxidized relatively slowly to generate CO. Only after all of the fuel was depleted by reaction, was the remaining oxygen rapidly consumed and CO oxidized to form CO_2 .

The calculations show that reaction takes place at temperatures greater than 700 K for all mixtures of combustion gases observed in Morehart's hood experiment with $\phi_g > 0.5$. For rich cases, except those having ϕ_g very close to 1, reaction leads to the depletion of all O₂ and the generation of CO. The increases in CO concentration are quite large, generally varying between 30 and 100%.

It was noted above that two well-defined temperature regimes were identified for the reaction behavior. At low temperatures very little hydrogen was generated and the primary hydrogen-containing product was water. At higher temperatures hydrogen becomes a major reaction product. The oxygen, which at lower temperatures forms water, is now free to react further with the fuel to generate additional CO. As a result, significantly higher concentrations of CO are generated at the higher temperatures than at the lower. A well-defined changeover in reaction behavior takes place between 1000 and 1100 K.

Analysis of the reaction mechanism showed that the reason for the temperature dependence of hydrogen formation was a change in the free radicals which dominate the reactions. At low temperatures OH and HO₂ are the most important radicals while at high temperatures H and OH are more dominant. As discussed in the earlier work,¹⁸ the high temperature reactions are much better characterized than the lower temperature reactions involving HO₂. Limited comparisons of calculations using three mechanisms—the Dagaut *et al.* ethylene oxidation mechanism,²² a more recent Daguat *et al.* methane oxidation mechanism,²⁸ and the mechanism employed by Morehart¹¹ based on one taken from Glassman's book²⁹—showed that the different mechanisms gave results which were in good agreement at higher temperatures, but that larger differences in reaction behavior were calculated for temperatures less than 1100 K. The variations at low temperatures were primarily the result of uncertainties for reaction rates involving HO₂. For this reason, care should be exercised when using the lower temperature calculations for any more than qualitative arguments.

Figure 3 compares the calculated CO concentration as a function of residence time for an isothermal mixture of hood gases ($\phi_g = 1.76$) assuming either infinitely slow (plug-flow reactor) or infinitely fast (psr) mixing. While there are minor differences in the time behavior and the ultimate levels of CO generated, the two sets of curves are in good agreement, demonstrating that the calculated behaviors are relatively insensitive to mixing conditions. On this basis, the calculations should



Fig. 3. Comparison of calculated CO mole fraction as a function of residence time for perfectly stirred (dashed line) and plug-flow (solid line) isothermal reactors having temperatures of 900 and 1200 K. $\phi_g = 1.76$. Initial concentrations taken from Morehart.¹¹



Fig. 4. Comparison of CO mole fraction as a function of time for a plug-flow reactor calculated assuming either adiabatic (solid lines) or isothermal (dashed lines) heat transfer conditions. Starting temperatures are 900 and 1200 K. $\phi_g = 1.76$. Initial concentrations taken from Morehart.¹¹

be appropriate for the upper layers in hood experiments where concentrations are generally found to be uniform for regions outside of the fire plume.

The calculations for the plug-flow and perfectly stirred reactors were done assuming both isothermal and adiabatic conditions. Comparisons of the results lead to very important conclusions concerning the reaction behavior of rich combustion gas mixtures. Figures 4 and 5 compare the results of calculated CO concentrations as a function of time for a plug-flow reactor with adiabatic and isothermal conditions and ϕ_g of 1.76 and 2.61. Results are shown for initial temperatures of 900 and 1200 K. Figure 6 shows the temperature variations for the adiabatic calculations. Note that, as expected for the oxidation of fuel, the initial rapid reactions lead to increases in temperature. The temperature increases for $\phi_g = 1.76$ are much larger than for $\phi_g = 2.61$ due to the higher concentration of O_2 in the starting mixture. Close inspection shows that at long times the high temperature mixtures are cooling very slowly. The reason for this observation is discussed below. Despite the increases in temperature, for the 900 and 1200 K cases shown in Figs 4 and 5, the two heat loss assumptions result in very similar time behaviors for the CO mole fraction, and the concentrations at long times are very nearly equal.



Fig. 5. Comparison of CO mole fraction as a function of time for a plug-flow reactor calculated assuming either adiabatic (solid lines) or isothermal (dashed lines) heat transfer conditions. Starting temperatures are 900 and 1200 K. $\phi_g = 2.61$. Initial concentrations taken from Morehart.¹¹



Fig. 6. Calculated temperatures are plotted as a function of residence time for an adiabatic plug-flow reactor having initial reactant temperatures of 900 and 1200 K. ϕ_g values are 1.76 (solid lines) and 2.61 (dashed lines). Initial concentrations are taken from Morehart.¹¹



Fig. 7. Comparison of CO mole fraction as a function of time for a plug-flow reactor calculated assuming either adiabatic (solid lines) or isothermal (dashed lines) heat transfer conditions. Starting temperatures are 1000 and 1300 K. $\phi_g = 1.76$. Initial concentrations taken from Morehart.¹¹

The CO concentration behaviors are very different for the isothermal and adiabatic cases when the initial temperatures are assumed to be 1000 and 1300 K, as can be seen in Figs 7 and 8 for $\phi_{o} = 1.76$ and 2.61. The amounts of CO generated are significantly higher for the adiabatic calculations for both of these initial temperatures. The final CO concentrations for the adiabatic calculations with initial temperatures of 1000 K approach the isothermal results for temperatures of 1300 K. This can be understood by considering the temperature history for these cases shown in Fig. 9. For both, the temperature rises significantly above 1000 K as the reactor residence time is increased. As discussed earlier, for the isothermal calculations, a modification in the dominant reaction pathway is found on going from 1000 to 1100 K. The increased CO production for the adiabatic calculations with initial temperatures of 1000 K is the result of this change in pathway which occurs as the temperature is increased. This is the reason why the final CO concentrations approach those for the 1300 K isothermal cases. Note that for the adiabatic calculations with an initial temperature of 900 K, the temperature rise is not large enough to induce the switchover in reaction pathway (see Figs 4, 5, and 6) except at the longest residence times for $\phi_g = 1.76$.

The reasons for the increased CO concentration for the adiabatic



Fig. 8. Comparison of CO mole fraction as a function of time for a plug-flow reactor calculated assuming either adiabatic (solid lines) or isothermal (dashed lines) heat transfer conditions. Starting temperatures are 1000 and 1300 K. $\phi_g = 2.61$. Initial concentrations taken from Morehart.¹¹



Fig. 9. Calculated temperatures are plotted as a function of residence time for an adiabatic plug-flow reactor having initial reactant temperatures of 1000 and 1300 K. ϕ_g values are 1.76 (solid lines) and 2.61 (dashed lines). Initial concentrations are taken from Morehart.¹¹



Fig. 10. Calculated concentrations of CO, CO₂, H₂, H₂O, CH₄, C₂H₄ and C₂H₂ are plotted as a function of residence time for an adiabatic plug-flow reactor having an initial temperature of 1300 K. $\phi_g = 2.61$. Initial concentrations taken from Morehart.¹¹

calculations with starting temperatures of 1300 K are more subtle and complex. Figures 7 and 8 show that following rapid increases in CO mole fractions for short residence times, the CO concentrations continue to rise slowly for longer residence times. Figure 9 indicates that the increases in CO concentrations at long residence times are accompanied by decreases in temperatures, which require that the overall reactions be endothermic. For the $\phi_{g} = 2.61$ calculation the temperature increase is small, ≈30 K. Analysis of the calculated reaction behavior shows that the principal reaction occurring in this case is the conversion of CH4 to ethylene and acetylene with an increase of the H₂ concentration. This can be seen in Fig. 10 where the concentrations of the important chemical species are plotted as a function of residence time. The small changes in CO, CO₂, H₂O concentrations for this case suggest that the elementary 'shuffle' reactions involving hydrogen atoms (H·), oxygen atoms (O:), and hydroxyl free radicals ($OH \cdot$),

$$\mathbf{H} \cdot + \mathbf{O}_2 \rightleftharpoons \cdot + \mathbf{O}: \tag{1}$$

$$O: + H_2 \rightleftharpoons OH \cdot + H \cdot \tag{2}$$

$$OH \cdot + H_2 \rightleftharpoons H_2 O + H \cdot \tag{3}$$

$$2OH \rightarrow H_2O + O:$$
 (4)

$$CO + OH \rightleftharpoons CO_2 + H \lor,$$
 (5)

responsible for bringing CO, H_2 , CO₂ and H_2O into thermodynamic equilibrium are relatively unimportant. This is likely due to the exceedingly low concentrations of O·, H·, and OH· for this rich, relatively low temperature case.

The $\phi_g = 1.76$ case is somewhat different as can be seen in Fig. 11 where the calculated concentration dependencies on residence time are shown for CH₄, CO, CO₂, H₂ and H₂O. Both CO₂ and H₂O are falling off with residence time, while H₂ and CO are increasing. Increases in C₂H₂ and C₂H₄ are relatively small in comparison to the $\phi_g = 2.61$ case. As will be shown shortly, these changes in concentrations are expected as Reactions (1)–(5) begin to equilibrate the major combustion products at high temperatures. The differences observed for the two ϕ_g values can be attributed to the higher temperatures achieved for the $\phi_g = 1.76$ calculation which allows low concentrations of the free radicals necessary for the reactions to be generated.

The results of these calculations have important implications with regard to the use of thermodynamic arguments to predict releases of combustion products by fires which will be discussed at the end of the following section.

Thermodynamic calculations

As noted previously, researchers at the California Institute of Technology⁹⁻¹¹ attempted to match their experimental measurements of hood gas concentrations by calculating predicted combustion product levels assuming thermodynamic equilibrium and searching for an appropriate freezing temperature to match the concentrations. The approach is made somewhat clearer by considering the results shown in Figs 12-14 where calculated equilibrium products of combustion are plotted as a function of temperature for three different initial starting mixtures (lean, near-stoichiometric, and rich) taken from the work of Morehart.¹¹ For any given temperature, equilibrium concentrations of products can be compared directly with the hood measurements. It should be noted that the calculated equilibrium mixtures are very similar to those obtained for starting mixtures of natural gas and air having the same equivalence ratios. The plots are for the major species CO, CO₂, H₂, H₂O, CH₄ and O₂. When these species do not appear on a plot it indicates that the missing concentrations are very low compared to the species which do appear. For instance, the equilibrium mole fractions of CH₄, CO and H₂ are very low for the lean case (see Fig. 12).

Two behaviors observed for the calculated equilibrium mixtures



Fig. 11. Calculated concentrations of CO, CO₂, H₂, H₂O and CH₄ are plotted as a function of residence time for an adiabatic plug-flow reactor having an initial temperature of 1300 K. $\phi_g = 1.76$. Initial concentrations taken from Morehart.¹¹



Fig. 12. Equilibrium concentrations of CO₂, H₂O and O₂ are plotted as a function of temperature for a mixture having $\phi_g = 0.81$. Equilibrium concentrations of CH₄, CO and H₂ are too low to appear on this scale. Input concentrations are taken from Morehart.¹¹



Fig. 13. Equilibrium concentrations of CO, CO₂, H₂ and H₂O are plotted as a function of temperature for a mixture having $\phi_g = 1.09$. Equilibrium concentrations of CH₄ and O₂ are too low to appear on this scale. Input concentrations are taken from Morehart.¹¹



Fig. 14. Equilibrium concentrations of CO, CO₂, H₂, H₂O and CH₄ are plotted as a function of temperature for a mixture having $\phi_g = 2.61$. Equilibrium concentrations of O₂ are too low to appear on this scale. Input concentrations are taken from Morehart.¹¹



Fig. 15. Equilibrium concentrations of CO are shown for mixtures over a range of ϕ_g from 0.50 to 2.81. Results are included for temperatures of 900, 1200, and 1500 K. Input concentrations are taken from Morehart.¹¹

should be noted. For the lean condition all fuel is consumed, and the only predicted equilibrium products are fully oxidized water and carbon dioxide. The situation is very different for the rich mixture. Products of incomplete combustion are predicted, and their concentrations increase dramatically with temperature. At the highest temperatures, calculated concentrations of CO and H_2 are found to be extraordinarily high. Unreacted fuel exists for temperatures below 1000 K, but very little is expected for the higher temperatures.

Figure 15 shows the behavior of equilibrium CO mole fraction as a function of ϕ_g for temperatures of 900, 1300 and 1500 K. The trends described above are clear. Note that concentrations are very low for lean conditions and that the formation of CO is favored as the temperature is increased. Equilibrium concentrations of CO for $\phi_g \gg 1$ are generally much higher than observed in the hood experiments.

DISCUSSION

The GER concept offers a very promising approach for predicting the generation of combustion gases during enclosure fires. Our primary interest is the generation of CO. Babrauskas *et al.* have considered the fire scenarios responsible for the majority of fire deaths involving CO.³

They conclude that the most common scenario, by far, is that of a fully developed fire (flashed over)³⁰ burning underventilated within an enclosure. The products of combustion, including high concentrations of CO, are transported from the fire room to remote locations where victims often succumb. Here we will focus on the implications of the GER concept for this type of fire.

The author has reviewed the results of a large number of full-scale fire tests carried out at NIST over a period of years. In general, upper-layer temperatures for fully developed fires which are burning underventilated are in the 1100–1300 K range. Note that these temperatures are much higher than observed in the hood experiments. Clearly, the dependence of the ϕ_g concentration correlations on temperature is of great concern.

The detailed chemical-kinetic calculations described above provide explanations and insights for many of the observations in the hood experiments. Conceptually, the chemical reactions responsible for the generation of combustion products can be viewed as taking place either in the fire plume itself or in the upper-layer gases located outside of the plume. In this view, the temperature effect observed in the hood experiments could result from shifts in the relative generation rates of species by the fire plume or by additional reactions taking place within the hood gases.

It has been found from the experiments that raising the temperature of the hood gases leads to a depletion of oxygen and increased concentrations of CO and CO₂. The most important observation is that concentrations of CO₂ are significantly increased as the hood temperature becomes higher, while the concentrations of CO remain nearly constant or only increase slightly. This is contrary to the expected behavior if the gas mixtures observed in the low-temperature hood experiments are simply introduced into a higher temperature environment. The detailed chemical-kinetic calculations clearly indicate that the formation of CO would be strongly favored, and the concentration of CO₂ would be expected to remain nearly constant.

It must be concluded that higher hood-gas temperatures lead to a modification in the generation rates of chemical species by the fire plume, with the result that the fuel is more fully oxidized than when temperatures in the hood are low. Since it is currently impossible to model the formation of chemical species in a quenched fire plume, this result suggests that it will not be possible to model the variations of GER concentration profiles with temperature. Experimentation will be required to characterize the effect.

The following picture emerges. When hood temperatures are low,

species generation rates by the plume are constant for a given ϕ_g and independent of temperature. The correlations only depend on the value of ϕ_g and the fuel. The detailed kinetic calculations are consistent with this conclusion since they indicate that the hood gases are essentially nonreactive for temperatures <700 K. As the upper-layer temperature is increased (>700 K), the species generation rates by the plume begin to change and more complete combustion takes place. Eventually, a temperature is reached for which all oxygen in the plume is depleted. If reactions among the product combustion gases do not take place (see the discussion of equilibrium effects below), no changes are expected within the hood gases and the product distributions should once again become independent of temperature.

Gottuk and coworkers^{25,31} have studied the formation of combustion products for fires within a reduced-scale enclosure especially designed to create an environment similar to that of the hood experiments. Air entered the enclosure through a vent at the bottom and was distributed throughout the length of the enclosure by a plenum system. Combustion gases exited the enclosure through a single window-type vent. Experiments showed that no air entered the exhaust vent. This configuration generated a very stable two-layer environment within the enclosure.

Values of ϕ_g were determined by measuring the air-inflow rate into the enclosure and the mass burning rate for the fuel. Upper-layer compositions outside of the fire plumes were very uniform. Concentrations of CO, CO₂, and O₂ were measured. Results for four fuels hexane, PMMA, wood, and a polyurethane foam containing 45% by weight of inert filler—were reported. Concentrations of the major combustion products were found to be correlated in terms of ϕ_g . These correlations held even during the transient development of the fires (i.e. when $\phi_p \neq \phi_g$).

Beyler⁵⁻⁷ had previously investigated three of the same fuels (C_6H_{14} , wood, and PMMA) considered by Gottuk and coworkers.^{25,31} The combustion gas concentrations in the hood and enclosure experiments were found to have similar correlations in terms of ϕ_g . In particular, the curves for CO in both experiments were found to have an 'S' shape with low concentrations for small ϕ_g , a transition region around $\phi_g \approx 1$, and much higher concentrations for high ϕ_g . However, the two curves were offset in ϕ_g by ≈ 0.5 with the hood CO concentration starting to rise at $\phi_g = 0.5$ and at $\phi_g = 1.0$ for the enclosure experiment. Concentrations of CO for rich conditions were slightly higher in the enclosure fires.

Comparison of the hood and enclosure fire results shows that for rich

conditions oxygen is found in the hood upper-layer gases while oxygen is absent for the enclosure fires. CO_2 concentrations for a given ϕ_g under rich burning conditions are considerably higher in the enclosure. For the rich fires, temperatures in the upper layer within the enclosure were all greater than 800 K (in a range of 800–1170 K). These are considerably higher than observed in the hood experiments (470– 800 K). The differences between the concentration behaviors in the hood and enclosure experiments are consistent with the temperature effect on the GER concept identified by Morehart and coworkers.^{11,12} These observations indicate that for this particular enclosure configuration the GER concept can be used to predict the generation of major combustion products when values of ϕ_g are known and allowances are made for the temperature effect.

Gottuk performed a detailed chemical-kinetic modeling investigation similar to that presented above.²⁵ The experimental case considered was for hexane fuel, but the modeling assumed that the unburned hydrocarbon could be represented by ethylene. The results of the calculations were very similar to those found in the current study. No reactions were calculated for temperatures <800 K. As the temperature was increased reactions began to take place. For rich conditions the reactions behavior was similar to that calculated above. The presence of the fuel inhibited the reaction of CO by suppressing free radical concentrations and competing successfully for the remaining radicals, and, as a result, CO was generated in preference to CO_2 by oxidation of the fuel. Oxygen concentrations were calculated to decrease, and, once depleted, reaction ceased. Gottuk recognized that the calculated changes were not consistent with experiment and hypothesized that higher temperatures changed the production rates for the plume instead of leading to further reaction in the gases outside of the fire plume.

As noted, researchers have previously attempted to understand the concentrations of combustion gases trapped above fires in terms of thermodynamic equilibrium predictions, however no single 'freezing' temperature could be identified which yielded good agreement. This observation can now be understood in terms of the kinetic and thermodynamics calculations. Comparison of the concentrations of CO calculated for temperatures in the range 1000–1300 K using detailed chemical-kinetic modeling and assuming thermodynamic equilibrium shows that chemical reaction yields nearly constant levels of CO at long times which are considerably less than predicted assuming full equilibrium. In fact, the only cases for which significant additional reactions were indicated following the initial, very rapid oxidation were the adiabatic calculations having initial temperatures of 1300 K (see Figs



Fig. 16. Calculated concentrations of CO, CO₂, H₂, H₂O and CH₄ are shown as a function of residence time for an isothermal plug-flow reactor at 1300 K. $\phi_g = 2.61$. Input concentrations are taken from Morehart.¹¹ Values shown on the right are the concentrations predicted assuming the mixture comes into full equilibrium at the indicated temperature.

7–9). Even in these cases, there was little conversion of CH_4 and CO_2 to CO as required to bring the system into full thermodynamic equilibrium. These calculations show conclusively that for temperatures <1300 K the products generated by combustion quenching in a rich upper layer are kinetically controlled and do not attain full chemical equilibrium.

Figures 16–18 compare the calculated behaviors of CH₄, CO, CO₂, H₂ and H₂O mole fractions for an isothermal plug-flow reactor as a function of residence time for temperatures of 1300, 1400, and 1500 K with $\phi_g = 2.61$ and a maximum residence time of 100 s. The concentrations of these species calculated assuming full chemical equilibrium are also indicated on the figures. The dramatic effect of temperature on the reaction behavior is clear. For the lowest temperature, after a rapid initial transient, slow reactions primarily convert CH₄ to H₂ and two-carbon hydrocarbons. Note that the H₂O concentration is little changed. Reactions are very slow and even after 100 s the concentrations are far from thermodynamic equilibrium (e.g. significant concentrations of CH₄ remain while Fig. 14 shows that the equilibrium concentration is essentially zero). At 1400 K the reactions are somewhat faster, but the concentrations calculated for a residence time of 100 s



Fig. 17. Calculated concentrations of CO, CO₂, H₂, H₂O and CH₄ are shown as a function of residence time for an isothermal plug-flow reactor at 1400 K. $\phi_g = 2.61$. Input concentrations are taken from Morehart.¹¹ Values shown on the right are the concentrations predicted assuming the mixture comes into full equilibrium at the indicated temperature.



Fig. 18. Calculated concentrations of CO, CO₂, H₂, H₂O and CH₄ are shown as a function of residence time for an isothermal plug-flow reactor at 1500 K. $\phi_g = 2.61$. Input concentrations are taken from Morehart.¹¹ Values shown on the right are the concentrations predicted assuming the mixture comes into full equilibrium at the indicated temperature.

are still far from equilibrium. Most significant is the observation that both H_2O and CO_2 have begun to disappear. This is an indication that a temperature has finally been reached for which the major combustion products are starting to come into thermodynamic equilibrium. It is the elementary reactions listed as Reactions (1)–(5) which must take place in order to generate the high CO and H_2 concentrations predicted by the equilibrium calculations for high-temperature rich mixtures. For the 1500 K case the calculated concentrations are beginning to approach equilibrium levels for a 100 s residence time. It should be noted that even for this high temperature, a long period is required for total thermodynamic equilibrium to be achieved.

These results indicate that the formation of combustion products by fires burning under fuel-rich conditions is normally a kinetically controlled process. Concentrations will approach thermodynamic equilibrium levels only for fires which are at much higher temperatures than typical of fully developed enclosure fires. Note that this conclusion means that it is inappropriate to use thermodynamic equilibrium calculations to predict upper-layer combustion products as proposed by Nakaya.²⁶

The work of Gottuk and coworkers^{25,31} has demonstrated that the major combustion gases in the upper layers of enclosure fires can be predicted using the GER concept when the fires burn in a configuration similar to that used for the hood experiments. It must be remembered that the enclosure used by these workers was not typical of most enclosure fires since the ventilation and exhaust pathways were independent and air was brought into the enclosure over a wide area at the base. It is certainly conceivable that if the ventilation and exhaust pathways are through the same opening(s), the mixing behavior can be much more complex, and that direct entrainment of air into the upper layer without passing through a flame zone might take place. In this case it would be expected that reactions similar to those calculated from the detailed chemical-kinetic models would occur. The concentrations of CO would be expected to increase above those predicted by the GER concept. Measurements in a $\frac{2}{5}$ -scale model of a standard fire test room^{32,33} at NIST have demonstrated just this behavior.³⁴ The enclosure has a single doorway through which both ventilation air inflow and combustion gas exhaust must occur. Measured upper-layer concentrations of combustion gases indicate that air enters the upper layer both by way of the fire plume (natural gas was the fuel) and by direct mixing into the upper layer with subsequent reaction to generate CO in preference to CO_2 in agreement with predictions of the kinetic modeling.

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The experimental and calculational results allow an assessment of the conditions for which the use of the GER concept can be used for predicting combustion products in the upper layers of enclosure fires.

Conditions where the GER concept is appropriate for predicting CO formation in enclosure fires

(1) Fires for which the upper-layer temperature is less than 700 K

The use of the GER concept is most appropriate for enclosure fires falling into this category. The upper layers are expected to be nonreactive. Both the hood experiments and the detailed chemical-kinetic modeling studies indicate this to be the case. Generation rates of combustion products as a function of ϕ_g are independent of temperature for this temperature range.

(2) Fires for which the upper layer is lean and very hot (>900 K) Fires falling into this category are expected to generate combustion products in amounts very similar to free-burning, fully ventilated fires. In general, CO levels are expected to be low unless the fuel generates unusually high levels of soot or is unusually stable.

(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) For this condition the fires will generate combustion products in the manner typical of hood fires having high temperatures over the full range of ϕ_g . With regard to CO, it has been shown that for $\phi_g > \approx 1.5$, yields are relatively constant and similar to those observed in lowtemperature hood experiments.

Conditions where the GER concept is inappropriate for predicting CO formation in enclosure fires

(1) Fires having $\phi_g > 0.5$ and intermediate temperatures (700–900 K) in the upper layer

Hood experiments have shown that for these conditions the relative generation rates for combustion products in the plume are dependent on the upper-layer temperature. Reactions within the upper layer itself are also possible and will be dependent on the layer residence time. The use of the GER concept for these conditions would be inappropriate.

(2) Fires for upper-layer temperatures > 900 K for which oxygen (air) enters a rich upper layer directly

Both detailed chemical-kinetic analysis and experiments indicate that for these conditions any oxygen which reaches the upper layer directly reacts with the rich gases to generate primarily CO as opposed to CO_2 . The concentrations of CO observed for these cases is higher than would be predicted based on the GER concept. It is possible that the GER concept can still be used to predict the generation rates of combustion gases by the fire plume, and that an additional model can be employed to predict the changes in concentration as the result of upper-layer reactions.

(3) Fires having upper-layer temperatures \gg 1300 K

For this case, which is expected to be rare for enclosure fires, the combustion gases will begin to come into full thermodynamic equilibrium. In this case the GER concept predictions will definitely fail since the products observed in the experiments on which the concept is based are kinetically controlled and far from equilibrium.

FINAL REMARKS

Experiments and analysis suggest that it may be possible to use the GER concept as a first step for calculating the generation of combustion gases in enclosure fires. However, it is clear that great care must be exercised and several limitations must be considered.

The GER concept is subject to a temperature dependence. Based on available evidence, this may not be a serious limitation in typical enclosure fires where upper-layer temperatures are generally lower than 1300 K, but higher than 1000 K.

The experiments which form the basis of the GER concept are for a very specific burning configuration—a single fire plume with air available from all sides at the fire base. An enclosure fire often has multiple fuel sources which have a range of access to the available air supply. Under these complicated conditions it is possible that the GER concept may not hold.

The GER concept is only expected to provide a prediction for combustion gases *within* the upper layer of the enclosure. Very little is known concerning the fate of the gases once they exit the enclosure. Additional burning may occur if the gases encounter an air source, or they may simply cool and be transported. Experimentation will be required to characterize these behaviors. The presence of fuel sources in the upper layer can severely alter the GER concept. In work to be discussed elsewhere, Pitts *et al.*³⁵ have shown that the pyrolysis of wood isolated in the high-temperature upper layer of an enclosure fire leads to the generation of extremely high levels of CO within the layer.

At the present time, the GER concept should be considered as a powerful, but limited approach for engineering estimates of the generation rates of combustion gases by enclosure fires. With particular regard to the formation of CO, the following should be kept in mind. GER concept predictions of CO formation should always be considered as the *minimum* possible. Three mechanisms have been mentioned which can lead to a breakdown in the GER concept predictions. In each case the result is the generation of additional CO beyond that predicted by the GER concept alone. In some cases the increases in CO concentration can be quite large.

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