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REACTIVITY OF PRODUCT GASES GENERATED IN IDEALIZED ENCLOSURE FIRE ENVIRONMENTS

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Previous experiments have demonstrated that the mole fractions of major product gases trapped in a hood located above a fire can be correlated in terms of the global equivalence ratio. Temperatures in the hood experiments have generally been low. Full-kinetic calculations are employed to characterize the reactivity and reaction behavior for the product gases observed in a hood experiment burning natural gas as fuel. A range of temperatures (700–1300 K) typical of enclosure fires is considered. Mixing is assumed to be infinitely fast (perfectly-stirred reactor) or infinitely slow (plug-flow reactor). Both isothermal and adiabatic cases are treated. Calculations are reported for a range of residence times (0–20 s) and global equivalence ratios (0.5–2.83). The dominant variable for reaction behavior is found to be temperature. Effects due to mixing and heat transfer assumptions are less important. The results indicate that the hood product gases are reactive for temperatures greater than 800 K. For rich mixtures, reaction generates primarily carbon monoxide as opposed to carbon dioxide. At higher temperatures the formation of hydrogen is favored over water while water is favored in the 800–1000 K range. In the lower temperature range HO_2 is the dominant free radical. Uncertainties in rates for reactions involving this specie introduce considerable uncertainty into the calculated behaviors. At higher temperatures (1100–1300 K) the important free radicals are H atom and OH. Reactions involving these radicals are better characterized than those involving HO_2. The findings suggest that the results of the hood experiments cannot be used directly for the modeling of species production 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 are poorly understood. A long-term program at the Building and Fire Research Laboratory seeks to develop an understanding of and predictive capability for the generation of CO in fires.[4]

Enclosure fires are often modeled as consisting of two layers in which burning occurs in a relatively low-temperature, unvitiated lower layer and the products of combustion are located in a hot upper layer which may be highly vitiated.[5] Researchers at Harvard University[6,7] and the California Institute of Technology[8–10] investigated the production of CO in idealized analogs of these models. Buoyancy-driven fires burning in an open laboratory were located beneath large hoods which trapped the combustion products. By changing the fuel release rate and the distance between the flame base and the hood the air entrainment and hence the global equivalence ratio (GER, symbolized as ϕ and defined as the mass ratio of fuel and air entering the hood normalized by the mass ratio required for stoichiometric burning) could be varied over a wide range. These experiments showed that concentrations of major combustion products trapped above a fire are well correlated by the GER. The correlations hold even when air is injected directly into the upper layer.[9,10] The existence of these correlations has been termed the *global equivalence ratio concept*. Figure 1, showing data taken from Morehart,[10] is an example of the GER concept for a natural gas flame.

If the GER concept were valid for enclosure fires it would provide a powerful means for predicting CO generation. One potential problem is that upper-layer temperatures in the hood experiments (measured for locations outside of the fire plume) are considerably lower (460–870 K, with the great majority less than 700 K)[6–10] than those observed in fully-developed room fires (typically 1200–1300 K).[11]

Two minimum requirements for the GER concept to hold for enclosure fires are that the generation rates of combustion products by the fire

plume remain unchanged from the hood experiments and that the upper-layer gases outside of the fire plume be nonreactive. In this work the second of these criteria is tested for a natural gas fire. Full-kinetic modeling, in conjunction with two idealized mixing models, is used to characterize the reactivity of the product gases generated in Morehart's experiments[9,10] for the temperatures typical of enclosure fires. The modeling approach and the calculated behaviors are the focus of this paper. The implications of the findings for the application of the GER concept to enclosure fires will be discussed in greater detail elsewhere.[12] It should be noted that, in a different context, Morehart made similar calculations, with a maximum temperature of 1034 K, for a single GER value.[10]

Modeling Approach

The system of interest here, a natural gas fire within an enclosure, is far too complicated to treat with existing reacting flow models. Instantaneous mixing rates, temperatures, and heat loss behavior are highly variable and uncharacterized. The approach adopted is to analyze the upper layer as a simplified reactor in which molecular heat and mass transport are unimportant and to bracket the possible effects of mixing behavior, temperature, and heat transfer. Full-kinetic modeling is used to characterize the reaction behavior of this idealized reaction system. An excellent introduction to full-kinetic modeling is provided by Westbrook and Dryer.[13] Only homogeneous (gas-phase reactions) reactions are considered. This approximation is reasonable since natural gas fires are known to generate low levels of soot.

Mixing Models:

The mixing behavior within an upper layer of an enclosure fire is poorly characterized. In order to assess the effects of mixing, calculations were done for two well-defined mixing limits-infinitely slow (plug-flow reactor) and infinitely fast (perfectly-stirred reactor) mixing.

Computer Programs and Calculational Procedures:

Researchers have developed a wide variety of computer programs for solving full-kinetics problems. Codes from the Combustion Research Facility of the Sandia National Laboratory were used. The Sandia approach is to build computer programs to solve particular problems from a series of routines, known collectively as CHEMKIN,[14] which perform basic bookkeeping and thermodynamic and kinetic analyses.

Sandia has provided codes for plug-flow and perfectly-stirred reactors. The programs used were SENKIN[15] for the plug-flow reactor and PSR[16] for the perfectly-stirred reactor. The reader is referred to these references and citations therein for details concerning the differential equations and solution methods. Both of the codes allow sensitivity analysis, a formal mechanism for identifying the key elementary reactions.

The FORTRAN codes were mounted on two computer workstations—a Masscomp 5450 and a Silicon Graphics 4D/20 Personal IRIS.* Software was written for simple analysis and display of the calculational results. In addition, the program SENKPLOT[17] developed at NIST was used to display the results of SENKIN calculations on the IRIS. Mole fractions, production rates, and sensitivity coefficients for individual reactions are all easily visualized allowing detailed analysis of reaction pathways.

Reaction Mechanisms:

Figure 1 shows that the starting mixtures will generally contain methane, ethane, acetylene, oxygen, nitrogen, water, hydrogen, carbon monoxide and carbon dioxide. The only previous modeling work identified which considered such complicated mixtures was the low temperature calculations of Morehart for a single ϕ.[10]

A large number of mechanisms for the oxidation of the one- and two-carbon species of interest have been published. Following a thorough literature review and some testing of alternate choices, a mechanism for the oxidation of ethylene developed by Dagaut et al.[18] was used. This mechanism was chosen since it had been recently updated with the latest available rate constants and was validated by comparison with jet-stirred reactor measurements at temperatures (880–1253 K) and equivalence ratios (0.15–4) similar to those of interest here. The chosen mechanism was developed in a hierarchial manner over a period of years and should be applicable for all of the fuel molecules of interest. Dagaut et al.[18] include species containing three and four carbon atoms in their full mechanism, but indicate that these are relatively unimportant. In the interest of simplicity, these reactions were omitted. The resulting mechanism consisted of thirty-one chemical species undergoing 183 reactions.

The mechanism includes the elementary reac-

*Certain materials and equipment are identified in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

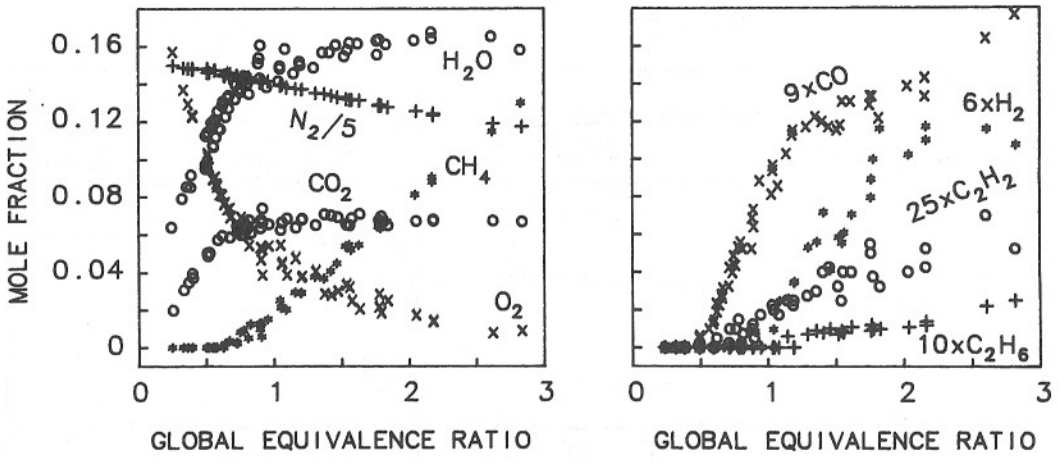

FIG. 1. Mole fractions of nitrogen, oxygen, water, carbon dioxide, methane, carbon monoxide, hydrogen, ethane, and acetylene measured in a hood above a natural gas fire plotted as a function of the global equivalence ratio in the hood. Data taken from tables in Morehart.[10]

tions and the corresponding coefficients for modified Arrhenius rate laws. Reverse reaction rates are calculated from equilibrium constants determined from appropriate thermochemical data. When available, coefficients for fits of the thermodynamic functions were taken from the Sandia compilation.[19] Values for those species not included in this compilation were taken from Senkan.[20]

Temperature, GER, and Residence Time Ranges:

Calculations were done for a temperature range of 700–1300 K. Initial temperatures for the gases are assumed to be the same as the reactor temperature. The lower part of this range corresponds to the highest temperatures observed in the hood experiments while the higher end is typical of fully-developed enclosure fires.

Morehart[9,10] has observed products of incomplete combustion for GERs greater than 0.5. The highest GER value he measured was 2.83. In the current work calculations were done for a series of GERs over the 0.5–2.83 range. Input mole fractions for the calculations were taken from tabulations of the combustion products measured in Morehart's experiments.[10]

The residence times of upper-layer gases within an enclosure are expected to vary widely. Calculations were made assuming residence times of 0 to 20 seconds.

Heat Transfer Behavior:

The heat transfer from a reacting upper layer of a fire is dependent on a large number of variables and is therefore generally poorly characterized. As in the case of mixing, calculations were done for two extreme limits—complete heat transfer (isothermal) and no heat transfer (adiabatic) to the surroundings.

Results

The wide range of parameters covered by the calculations precludes discussion of all results. Representative cases for the isothermal plug flow reactor are emphasized. The effects of mixing rate and heat transfer are assessed in the next section.

Figure 2 shows the time behavior of major reactant and product species as a function of time for temperatures of 800 K and 1300 K and $\phi = 2.17$. Figure 3 is a similar plot for $\phi = 1.09$. The very different reaction behaviors seen in Figs. 2 and 3 are striking. For both GERs reactions are observed at high and low temperatures. As expected, the overall reaction rate is much faster at 1300 K. For the rich case, reaction produces the partially oxidized product CO and very little additional CO_2. The relative increase in CO concentration is much larger at the higher temperature. Interestingly, hydrogen, which is generally considered to be a highly reactive fuel, does not disappear in either case. In fact, at the higher reactor temperature its mole fraction nearly doubles, while it only marginally increases at the lower temperature. The near-stoichiometric reaction initially produces partially oxidized products as well. At the high temperatures, however, the organic fuels are eventually depleted and a rapid conversion of H_2 and CO to water and CO_2 then occurs. This does not take place at

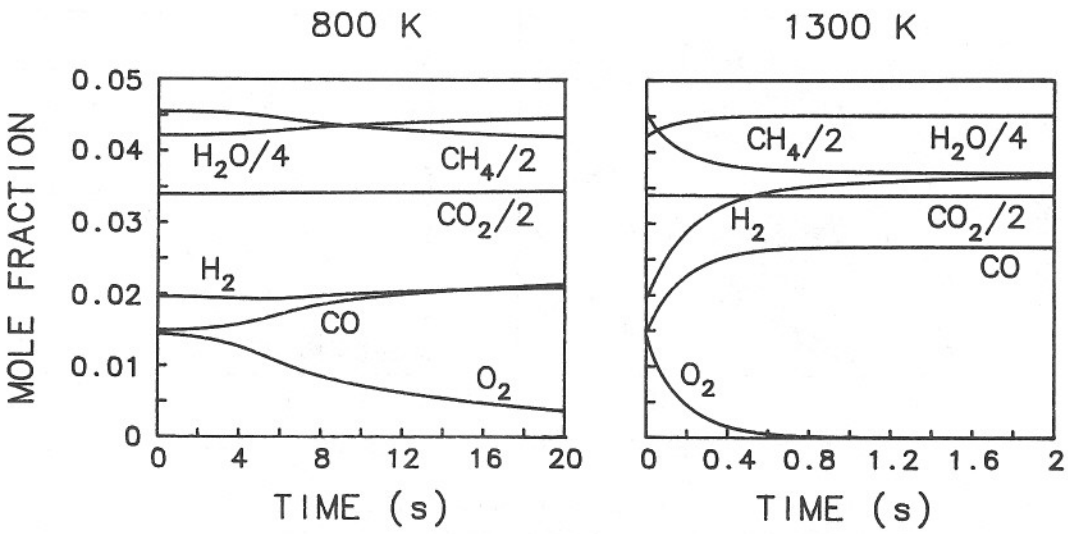

FIG. 2. Calculated time behavior of major gas species mole fractions for an isothermal plug-flow reactor as a function of residence time for $\phi = 2.17$. Results for 800 K and 1300 K are shown. Note the shorter time scale for the higher temperature. Initial mole fractions: nitrogen (0.62), oxygen (0.014), water (0.17), carbon dioxide (0.068), methane (0.091), carbon monoxide (0.015), hydrogen (0.020), ethane (0.0014), and acetylene (0.0017).

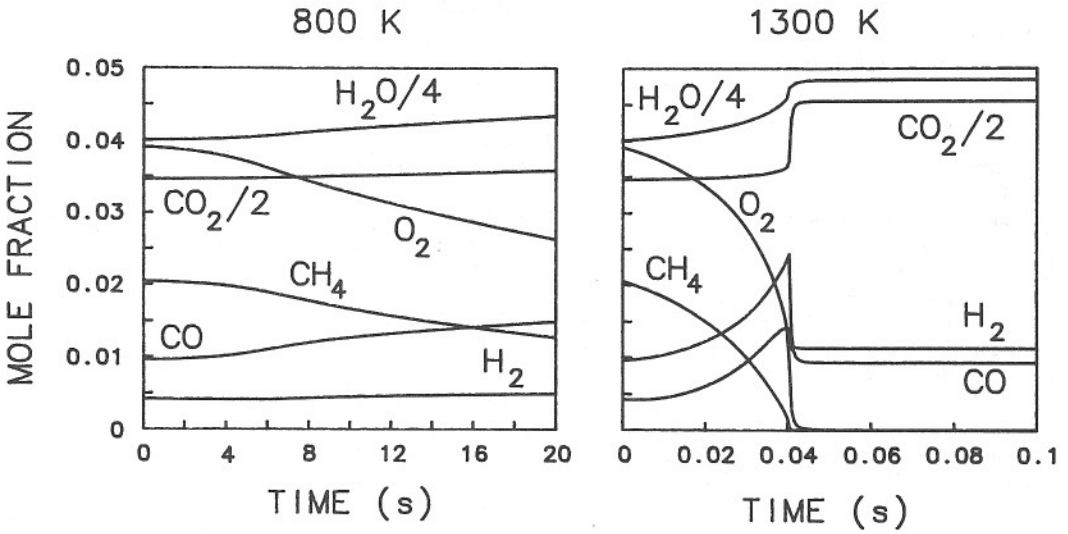

FIG. 3. Calculated time behavior of major gas species mole fractions for an isothermal plug-flow reactor as a function of residence time for $\phi = 1.09$. Results for 800 K and 1300 K are shown. Note the shorter time scale for the higher temperature. Initial mole fractions: nitrogen (0.69), oxygen (0.039), water (0.16), carbon dioxide (0.069), methane (0.020), carbon monoxide (0.010), hydrogen (0.004), and acetylene (0.0007).

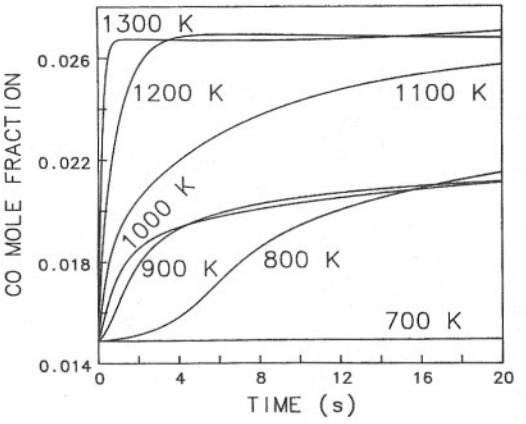

FIG. 4. Calculated carbon monoxide mole fractions for an isothermal plug-flow reactor as a function of time for the temperatures indicated. ϕ = 2.17. Initial concentrations the same as in Fig. 2.

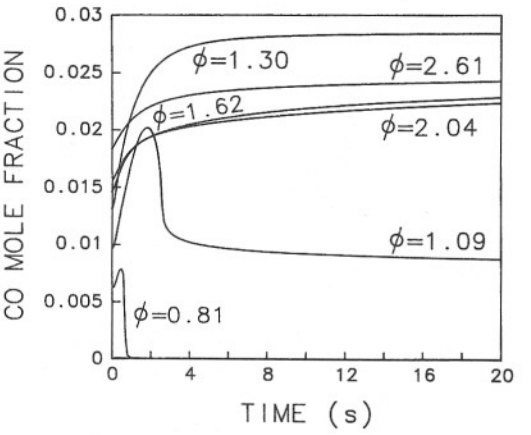

FIG. 5. Calculated carbon monoxide mole fraction for an isothermal plug-flow reactor at 1000 K as a function of time for the global equivalence ratios indicated. Initial concentrations are taken from Morehart.[10]

800 K since the oxygen is not completely consumed during the 20 s residence time.

Figure 4 shows plots of CO mole fraction as a function of time over the 700–1300 K temperature range for ϕ = 2.17. Note that there are three distinct regimes. At 700 K very little reaction occurs. In the 800 to 1000 K range the rate of reaction increases with temperature, but the ultimate mole fraction of CO generated at long times is roughly constant. Between 1000 and 1200 K there is a transition in the behavior and considerably higher levels of CO are produced. For the highest temperatures the reaction rates are quite fast and the ultimate levels of CO are again roughly constant, but considerably higher than in the 800–1000 K range.

Figure 5 shows a plot of CO concentration as a function of time over a range of ϕ for a reactor temperature of 1000 K. The ultimate level of CO generated is a strong function of ϕ with very low mole fractions observed for $\phi < 1$ while the largest fractional increase is for ϕ = 1.30.

Discussion

Isothermal Plug-Flow Reactor:

The calculations show that the gas mixtures observed in the hood experiments react very slowly at 700 K. This is consistent with the GER concept. By the time the temperature has reached 800 K, slow reactions are beginning to occur. Oxidation reactions take place in a series of stages. The organic fuels are oxidized at the earliest times. At lower temperatures acetylene reacts faster than methane or ethane. At the higher temperatures the rates of reaction are comparable for all three organic fuels. In the lower temperature range the primary products of the organic oxidation are CO and H_2O. For temperatures greater than 1100 K the principal products become CO and H_2.

For lean conditions, i.e. $\phi < 1$, rapid oxidation of CO and H_2 occurs once the organic fuels are depleted and the system approaches full oxidation. For ϕ values slightly greater than one the organic fuels are first depleted and then a relatively rapid oxidation of CO and H_2 continues until all of the oxygen is depleted. For ϕ = 1.30 the concentration of O_2 is not high enough to oxidize significant amounts of H_2 and CO and the highest conversion of fuel to CO is observed.

The calculated behaviors can be understood by considering the major reaction pathways. Figure 6 shows the chemical routes for ϕ = 1.76 and temperatures of 900 and 1200 K. At 900 K the instantaneous pathway is that for the residence time of most rapid CO formation (0.85 s) while the higher temperature case is for a residence time of 0.1 s. At low temperatures a significant fraction of the total oxidation is due to reaction of C_2H_2. This suggests that the free radicals necessary to drive the reactions result from this oxidation. Once the C_2H_2 is depleted the oxidation of the saturated hydrocarbons occurs much more slowly. This conclusion was confirmed by rerunning the calculation in the absence of an initial C_2H_2 concentration. At 800 K there was essentially no reaction while for 900 and 1000 K the overall reaction rates were greatly re-

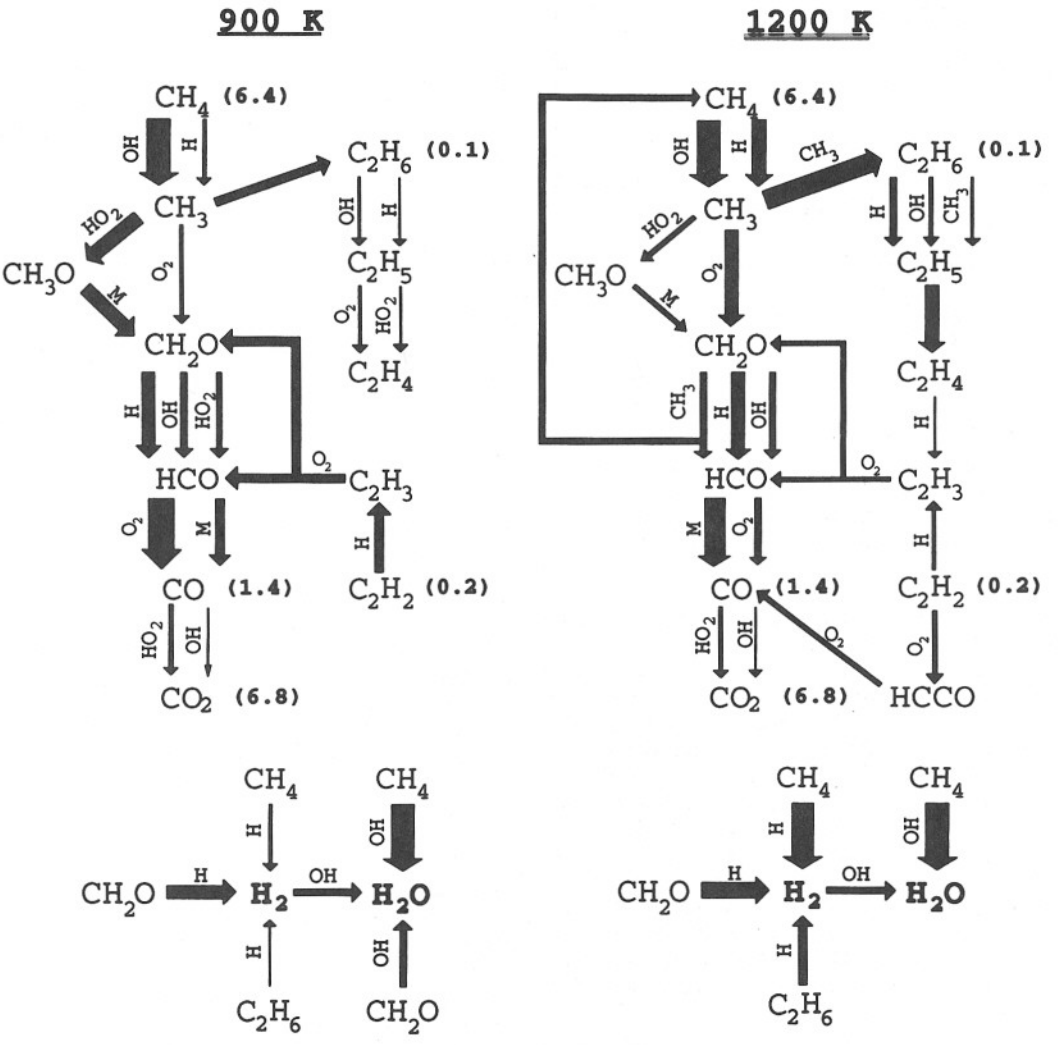

FIG. 6. Major reactive pathways in the plug flow reactor for temperatures of 900 K and 1200 K. ϕ = 1.76. Upper panels represent major oxidation routes while the lower panels emphasize the formation of hydrogen and water. Pathways are for single residence times: 0.85 s at 900 K and 0.1 s at 1200 K. Values in parentheses are initial mole fractions. The widths of the arrows are proportional to reaction rates. For the upper panels the maximum reaction rates are 3.7×10^{-3} mole/cm^3-s at 800 K and 2.2×10^{-2} mole/cm^3-s at 1200 K. Corresponding values in the lower panels are 3.4×10^{-3} mole/cm^3-s and 2.2×10^{-2} mole/cm^3-s.

duced. At 1200 K the relative contribution of the C_2H_2 reaction is much less and its presence has little effect on the overall oxidation process.

Figure 6 also shows that the free radicals responsible for oxidation change with temperature. At 900 K the HO_2 radical is most important. Sensitivity analysis shows that many HO_2 reactions have large sensitivity coefficients. At 1200 K reactions with H and OH are much more important. This change in the reaction pathway is particularly evident for the oxidation of methyl radical. The increased importance of the $CH_3 + O_2$ reaction at the higher temperatures is a primary reason for the more rapid oxidation.

The formation behaviors of H_2 and H_2O at 900 and 1200 K are also shown in Fig. 6. The enhancement of the relative formation rate for H_2 at the higher temperature is evident. It is due primarily

to the increased importance of reactions involving H atoms and, in particular, the relative increase in their reaction rate with CH_4.

From Fig. 6 it is clear that the oxidation of CO and H_2 is much slower than the oxidation of the organic fuels. This is an example of the well known self-inhibiting effects of organic fuel molecules. The free radicals necessary to promote reactions (here H, OH, and HO_2) are considerably more reactive with hydrocarbons than with CO or H_2, and, as a result, concentrations of free radicals remain quite low and the hydrocarbon fuels are only partially oxidized. When the hydrocarbons are depleted, the radical concentrations grow and the oxidation of CO and H_2 proceed rapidly as demonstrated in Figs. 3 and 5.

Effects of Changes in Mixing and Heat Transfer:

The calculations were performed for four conditions: isothermal plug-flow, adiabatic plug-flow, isothermal perfectly-stirred, and adiabatic perfectly-stirred reactors. In general, the trends revealed by the isothermal plug-flow reactor case were reflected in the other cases.

The generation of CO in the isothermal perfectly-stirred reactor showed similar trends to the isothermal plug-flow case. At 700 K there was essentially no reaction. In the 800–1000 K range roughly constant levels of CO were observed at long residence times. Above 1100 K much higher concentrations of CO were generated. The absolute concentrations and dependencies on residence time differed somewhat between the two types of reactors, but the variations were relatively minor.

The effects of varying the heat transfer behavior were dramatic and varied. As observed in the isothermal cases there was essentially no reaction at 700 K for adiabatic conditions. For temperatures of 800 K and above reaction did occur. As expected, temperature increases were observed for the oxidation reactions. The temperature rises were strong functions of ϕ with a peak increase for $\phi = 1.09$ for which the rise was on the order of 400 K. As ϕ was increased or decreased the temperature increases were much smaller. For $\phi \leq 0.81$ and ≥ 1.62 the observed rises were less than 200 K decreasing to near zero at the extreme values of ϕ.

The principal effects of the temperature increases on the reaction behavior are consistent with the isothermal findings. For initial temperatures of 800–1000 K the reactions are significantly accelerated. If the final temperature falls below 1100 K the ultimate level of CO generated is nearly the same as observed in the corresponding isothermal case. When the final temperature rises above 1100 K the transition in reaction behavior occurs and higher levels of CO, consistent with the high temperature isothermal results, are generated. It is possible for the final temperature to rise significantly above 1300 K when the initial temperature is high. For these cases it was found that the water gas shift reaction,

$$CO + H_2O = CO_2 + H_2,$$

starts to come into equilibrium. The formation of CO from CO_2 is thermodynamically favored and there are further increases in CO mole fraction with a corresponding drop in temperature.

It is concluded that mixing has a relatively small effect on reaction behavior as compared to temperature. The degree of heat transfer clearly affects the calculated reaction behavior. However, its effects can be understood in terms of the isothermal reaction behavior.

Sensitivity to Reaction Mechanism:

A detailed tuning of reaction mechanism is beyond the scope of this investigation. Some insights as to effects of changes in mechanism can be derived by comparing calculations using different literature mechanisms. In addition to the Dagaut et al. ethylene oxidation mechanism,[18] two others were considered. Initial calculations were done with the mechanism used by Morehart.[10] This is a modified version of a mechanism in Glassman's book.[21] Near the end of this study, Dagaut et al.[22] published a mechanism specifically tuned for the oxidation of methane. Several calculations were run using this new mechanism.

Figure 7 compares the calculated behaviors of CO concentration for $\phi = 1.76$ at 900 K and 1200 K using the three mechanisms. At the higher temperatures the behaviors are very similar. In each case the available oxygen is consumed and minor differences in the CO concentration are due to the final products distribution among H_2, H_2O, CO, and CO_2.

The behavior in the lower temperature range is considerably more complex. Analysis of the mechanisms suggests the variations are due to differences in the rates of reactions involving HO_2. Much of the difference between the two Dagaut et al. mechanisms[18,22] is attributable to a change in the rate law for

$$CH_3 + HO_2 = CH_3O + OH.$$

The rate constant at 900 K has been reduced by a factor of eight in the later mechanism.

The variations in behavior between the Morehart[10] and Dagaut et al.[18] mechanisms are due primarily to differences in rate laws for the following reactions:

$$HO_2 + HO_2 = H_2O_2 + O_2$$
$$H_2O_2 + M = OH + OH + M$$
$$CH_4 + HO_2 = CH_3 + H_2O_2.$$

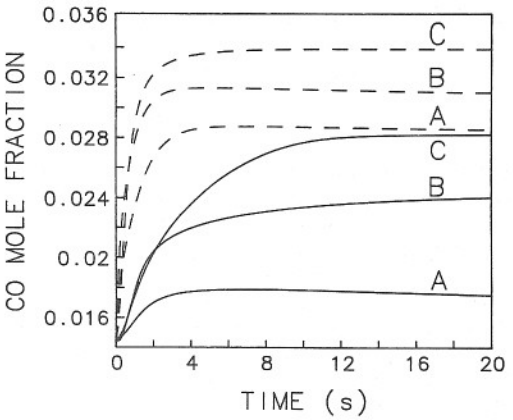

FIG. 7. Carbon monoxide mole fraction plotted as function of time for an isothermal plug flow reactor using three reaction mechanisms taken from the literature: A) Dagaut et al.'s methane oxidation mechanism,[22] B) Dagaut et al.'s ethylene oxidation mechanism,[18] and C) Morehart's mechanism.[10] Solid lines represent reactor temperatures of 900 K and dotted lines reactor temperatures of 1200 K.

In each case the rate laws used by Dagaut et al.[18] are preferred since they have been updated based on the latest experimental and theoretical analyses.

One investigation has been identified in the literature which is directly relevant to the reaction behavior in the 800–1000 K temperature range. Reid et al.[23] developed a kinetic model to describe the ignition of methane for temperatures on the order of 900 K. They provided a reaction flow diagram which looks very much like that shown in Fig. 6. In particular, they concluded that the $CH_3 + HO_2 = CH_3O + OH$ reaction dominates the oxidation of CH_3.

The mechanism comparison suggests that the reaction behavior for temperatures above 1100 K is fairly well understood and that predictions are likely to agree well with experimental behaviors. The predictions for the 800–1000 K range are much less certain. This will remain the case until a better understanding of the key elementary reactions in this temperature range becomes available.

Conclusion

These calculations have shown that the combustion gases observed in a hood located above a burning fire become reactive for temperatures above 800 K. For lean conditions these reactions lead to complete oxidation of fuel and partially oxidized molecules. The reaction behavior of rich mixtures is more complex. For temperatures above 1100 K the reactions of rich mixtures consume the available oxygen and produce significant amounts of CO, H_2, and H_2O. In the lower temperature range the degree of reaction involves complicated interactions between the oxidation of the relatively easily oxidized C_2H_2 and saturated fuels. There are large variations in the calculated behaviors due to uncertainties in the rate laws for the dominant reactions. In this temperature regime oxidation of rich mixtures leads preferentially to the formation of CO and H_2O.

The combustion gases observed in hood experiments become reactive for temperatures typical of fully-developed fires. Clearly, it will not be possible to extend the GER concept to enclosure fires without modification. This point will be discussed in detail in a later publication.[12]

Acknowledgements

The author would like to thank Dr. Donald Burgess (NIST) for providing the program SENKPLOT and Dr. Thomas Norton (formerly of NIST, now with Morgantown Energy Technology Center, Morgantown, WV) for many helpful discussions.

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COMMENTS

Richard G. Gann, National Institute of Standards and Technology, USA. We should note that the U. S. fire incidence data indicates that most fire deaths occur in fires that have proceeded beyond flashover. These fires have upper layer temperatures well in excess of the 700 K in the referenced hood experiments and in the reactive range studied in the paper. Thus, it can be generalized that one should not expect accurate predictions of CO yield based soley on the global equivalence ratio.

Author's Reply. This point is well taken. In the introduction to the paper it is stated that "fully-developed room fires" typically have temperatures in the 1200–1300 K range. Even though not explicitly stated, these fires are generally flashed over. It is recognized that a flashed-over, underventilated enclosure fire with transport of combustion gases away from the fire to other areas of a building is a very important scenario for fire deaths resulting from carbon monoxide. The high reactivity of the rich gas mixtures observed in the hood experiments does suggest that predictions of CO yield based solely on the global equivalence ratio should be made with great care.

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M. A. Delichatsios, Factory Mutual Research Corp., USA. This is a very valuable work which delineates the applicability, at high ceiling layer temperatures, of universal relationships for species concentrations (e.g., CO) in terms of mixture fraction. How does the author feel about the comparative (to this work) importance of CO yield variability with geometry, e.g., wall fires, ceiling fires, fires impinging on ceiling?

Author's Reply. The principal motivation of this study was to investigate the suitability of the state relationships observed in the hood experiments for predicting carbon monoxide in enclosure fires. The findings suggest that great care should be exercised. Ongoing experimental work at NIST on CO formation in a reduced-scale room suggests that configuration is indeed important. Unforunately, it appears that it will be necessary to include geometry effects in any engineering correlations which are developed for the prediction of CO formation in enclosure fires.

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R. F. Chaiken, US Bureau of Mines, Pittsburgh Research Center, USA. In some past studies of tunnel fires at the Bureau, in which the fuel consisted of a lining of coal, the amount of CO generated when the fire went fuel-rich approached about 20%. This is a factor of 10 greater than your studies using gaseous fuel. I believe the tunnel fires might be more representative of fully developed fires in real enclosures.

Author's Reply. The work presented here was of a limited nature and was intended to characterize the reactive behavior of the upper-layer gases observed in the hood experiments. Other ongoing efforts at NIST have indicated that mechanisms (other then the simple quenching of a turbulent fire plume upon entering a rich upper layer) do lead to sig-

nificantly higher concentrations of CO than observed in the hood experiments. The levels of CO cited by Dr. Chaiken are much higher than typically observed in full-scale enclosure fires. Without additonal information concerning the mechanism responsible for the high levels of CO observed in the tunnel fires, it is impossible to conclude whether or not similar mechanisms lead to high CO concentrations in tunnel and enclosure fires.

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Richard J. Roby, Virginia Polytechnic Institute and State University, USA. We have calcualted similar increases in upper layer CO at higher temperatures using the data of Morehart or Beyler at $\phi > 1.0$. However, experimentally in compartment fire measurements we have observed lower CO concentrations for several different fuels than Beyler or Morehart in the $1.0 \leq \phi \leq 1.5$ region.[1] This is contrary to both our modeling and your results presented in this paper.

REFERENCE

1. Gottuk, D. T., Roby, R. J. and Beyler, C. L.: Carbon monoxide production in compartment fires, to be published in the Journal of Fire Protection Engineering, 1992.

Author's Reply. The calculations reported here were designed to answer a very specific question: Are the upper-layer gases observed in the low-temperature hood experiments reactive at the temperatures typical of fully-developed room fires? The calculated behaviors are those expected when the fuel-rich gases observed in the low temperature hood experiments are suddenly introduced into a high temperature environment. As discussed in the introduction, in order for the calucated behaviors to be actually observed in an enclosure fire, it is also necessary for the concentrations of gases generated by the fire plume entering the upper layer to be unchanged from those generated in the low-temperature hood experiments. The observation of lower CO concentration in the 1 to 1.5 global equivalence ratio range cited by Professor Roby suggests that these production terms are significantly modified for the fire plumes entering higher temperature upper layers. It is currently not possible to model this extremely complex phenomenon, but the author does not find it surprising that such a dependence of generation rates on temperature is observed.