Twenty-Fifth Symposium (International) on Combustion/The Combustion Institute, 1994/pp. 1455–1462

CARBON MONOXIDE FORMATION IN FIRES BY HIGH-TEMPERATURE ANAEROBIC WOOD PYROLYSIS

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Building fire fatalities often occur at locations remote from the room where the fire is actually burning. The majority of these fire deaths are the result of smoke inhalation, primarily due to exposure to carbon monoxide (CO). Although causing nearly 2500 deaths per year in the United States, the mechanisms for the formation of CO in building or enclosure fires remain poorly characterized.

In order to test the hypothesis that high concentrations of CO can be generated by pyrolysis of wood in a high-temperature, vitiated environment, a series of natural gas fires, ranging from 40 to 600 kW in heat release rate, were burned inside a reduced-scale enclosure (RSE). The ceiling and upper walls of the RSE were lined with 6.4-mm-thick plywood. During each burn, the concentrations of CO, CO_2, and O_2 were monitored at two locations within the upper layer. Oxygen calorimetry was used to monitor the total heat release rate for each fire. Vertical temperature profiles for two positions within the enclosure were also recorded.

Much higher levels of CO were generated with the wood-lined upper layer than with comparable fires fueled only by natural gas. Volume concentrations as high as 14% were observed. The fires with wood in the upper layer had higher heat release rates and depressed upper-layer temperatures. The major conclusions of this work based on the experimental findings are (1) the pyrolysis of wood in a highly vitiated, high-temperature environment can lead to the generation of very high concentrations of CO in enclosure fires; (2) the overall wood pyrolysis is endothermic for the experimental conditions studied; and (3) the maximum mass loss rate of wood under the experimental conditions is on the order of 10 $gs^{-1}\ m^{-2}$ with the majority of released carbon being converted to a roughly 1:1 mixture of CO and CO_2.

Introduction

The majority of fire deaths within buildings [1] occur as the result of smoke inhalation from "flashed over" [2] fires at locations remote from the fire itself. Postmortem analysis of fire victims [3] as well as studies of the causes of fire death reported by medical examiners [4] indicate that roughly two-thirds of all building fire deaths are the direct result of exposure to the carbon monoxide (CO) generated by the fire. Although this represents nearly 2500 deaths per year in the United States [5], very few systematic investigations of CO formation during enclosure fires have been reported, and the mechanism(s) for generating CO in such fires remain poorly characterized.

Earlier idealized experiments [6–8] in which fires burning in an open laboratory were quenched upon entering a hood containing combustion gases showed that concentrations of the combustion gases, including CO and fuel, could be correlated in terms of the global equivalence ratio (GER), ϕ_g, which is defined as the mass of material in the upper layer derived from fuel divided by the mass of material derived from air normalized by the fuel to air ratio required for stoichiometric burning. The existence of these correlations has been termed the "global equivalence ratio concept" [9].

Gottuk et al. [10] demonstrated that the concentrations of combustion species generated within an enclosure carefully designed to create an environment similar to the hood experiments were also well correlated with ϕ_g, even though the correlations differed slightly from the hood results due to higher upper-layer temperatures in the enclosure fires. Work reported by Bryner et al. [11] and discussed by Pitts [12] demonstrated that the GER concept can breakdown when air is entrained directly into the upper layer of an enclosure with a single doorway. Even in the latter case, however, observed CO concentrations for underventilated burning were only 50% higher than predicted by the GER concept.

In 1987 in Sharon, PA, there was a fatal townhouse fire, where deaths occurred on the second floor, even though the fire was essentially localized in a first floor kitchen. One of the victims had an extraordinarily high level of carboxyhemoglobin, suggesting exposure to very high concentrations of CO. Levine and Nelson [13] investigated this fire in detail and

decided to simulate it in the full-scale burn facilities at the National Institute of Standards and Technology (NIST).

In order to simulate the wood paneling and cabinets in the kitchen, a heavy fuel loading of wood, 184 kg, was used. Concentration measurements of CO and other flame gases were made at the soffit of a doorway located at the base of a stairway leading to the second floor as well as in a "bedroom" located on the second floor. Volume concentrations of CO as high as 8% were observed downstairs, while concentrations in the upstairs bedroom exceeded 4%.

Beyler [7] had burned wood in a "hood" experiment and found that CO volume concentrations of 3.2% were generated during underventilated burning. Similar results were reported by Gottuk et al. [10] for their idealized enclosure. Concentrations of CO observed in the Sharon fire test are, therefore, at least 2.5 times higher than predicted by the GER concept. Such a large difference cannot be attributed to a temperature effect or entrainment of air directly into the upper layer. Another mechanism for CO generation must exist.

In this paper, it is shown that direct pyrolysis of wood in highly vitiated (anaerobic), high-temperature flame gases generates very high concentrations of CO, thus providing a likely explanation for the failure of the GER concept to predict the generation of CO during the Sharon fire test. Despite an extensive literature on the pyrolysis and burning behavior of wood and similar substances, we have found no experimental investigations of wood pyrolysis for the conditions of interest to this investigation. However, there are numerous studies in the literature suggesting that wood can be efficiently converted to CO when small particles are exposed to high temperatures under anaerobic conditions.

Milne [14] summarizes a number of experiments in which wood and related substances were rapidly pyrolized at high temperatures in inert environments. Many of these studies reported significant mass conversion to carbon oxides with the CO to CO_2 ratio being generally greater than one. Brink et al. [15] studied wood particle decomposition in a flow reactor over a 300 °C to 900 °C temperature range. The degree of conversion to gas increased with temperature as did the $CO:CO_2$ volume ratio. For 600 °C, this ratio was nearly 1 and increased to 12 by 900 °C. Arpiainen and Lappi [16] reported similar findings for the flash pyrolysis of pine bark with high conversion to carbon oxides and a $CO:CO_2$ ratio of 1 near 600 °C and of 4 for 800 °C.

Experimental

The experiments were performed in the reduced-scale enclosure (RSE) test facility at NIST. This facility is described fully elsewhere [11] and will only be summarized here. The RSE is a two-fifths-scale model of a standard full-scale room widely used for fire testing [17,18]. The RSE has inside dimensions of 0.98-m wide × 0.98-m tall × 1.46-m deep and a single doorway, which is 0.48-m tall × 0.81-m wide. The inside of the enclosure is lined with two layers of 1.27-cm-thick calcium-silicate boards, which are supported by a steel framework.

A 15.2-cm-diameter burner is positioned in the center of the RSE 15.2 cm above the floor. The flow rate of the fuel, natural gas, to the burner is monitored using both a diaphragm test meter and rotameters. The burner is ignited by a small propane pilot flame. Flow rates are adjusted to provide a range of fire sizes (assuming complete combustion and using heats of combustion based on the known composition of the natural gas) up to 600 kW.

Gas concentrations within the RSE are monitored at two locations by continuously extracting samples through 0.95-cm-diameter tubing and, after drying, using nondispersive infrared analyzers (CO and CO_2) and paramagnetic analyzers (O_2). Gas sampling locations are 10 cm from the ceiling (well within the upper layers of the fires). The front sample probe is 10 cm from the front wall that contains the door and 29 cm from a side wall. The rear sample probe is located 29 cm from the side and rear walls. Temperatures are recorded at several heights using two thermocouple trees placed in the front and rear of the enclosure at locations 20.3 cm from the side and end walls.

The RSE is placed under the large hood of the NIST furniture calorimeter [19], which utilizes oxygen calorimetry [20] to measure the heat release rate (HRR) of a fire. Note that measured HRRs reflect burning both inside and outside of the enclosure.

The results of an extensive series of natural gas burns are discussed elsewhere [11,12]. These earlier studies found that the natural gas fires became underventilated for HRRs greater than 200 kW. As the fires became underventilated, the concentration of CO observed in the upper layer increased quickly with fire size, reaching asymptotic values of approximately 2 and 3 vol.% in the rear and front of the enclosure, respectively. Upper-layer temperatures were quite high and also were found to differ in the front and rear of the enclosure (typically 1000 °C in the front and 850 °C in the rear). For underventilated burning, oxygen concentrations were very close to zero as expected for well-mixed rich gases at these temperatures [9,12,21].

For the current study, the ceiling and upper walls (36 cm down from the ceiling) of the RSE were lined with 6.4-mm-thick Douglas fir plywood in order to test the hypothesis that pyrolysis of wood in high-temperature, anaerobic environments can generate high concentrations of CO. The total mass of wood was approximately 10 kg. Natural gas fires of various sizes were then burned, and the concentrations of

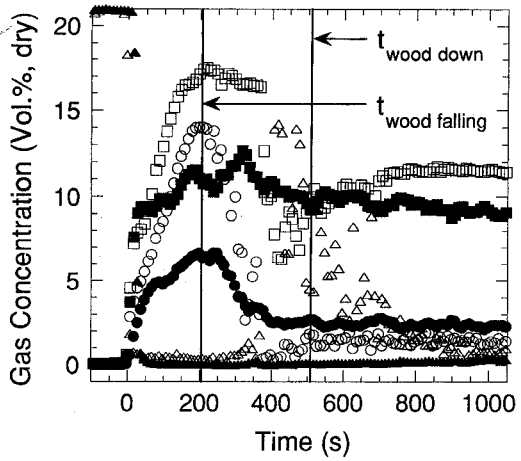

FIG. 1. Volume concentrations (dry) vs time for a fire within the RSE fueled by a natural gas flow corresponding to 400 kW and a plywood lining on the ceiling and upper walls. Results for CO (○, ●), CO_2 (□, ■) and O_2 (△, ▲) are shown. Samples were measured at front (filled symbols) and rear (open symbols) locations. The fire was ignited at time = 0 s. Times for when the wood first began to fall from the ceiling and walls and for when the wood had collapsed are indicated.

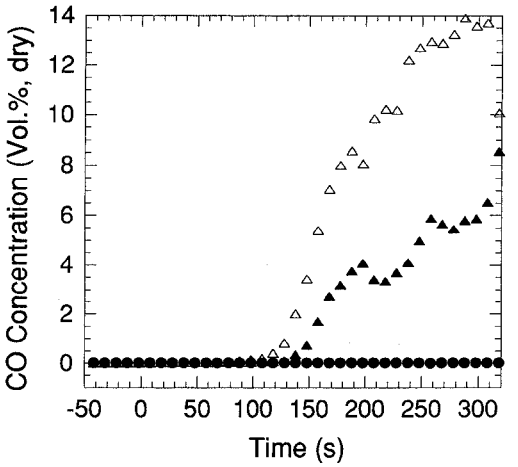

FIG. 2. Volume concentrations (dry) of CO vs time for a 50-kW natural gas fire (○ = rear; ● = front) and for a 50-kW natural gas fire with a plywood lining on the ceiling and upper walls (△ = rear; ▲ = front). The fire was ignited at time = 0 s, and the wood began to fall at 320 s.

CO, CO_2, and O_2 were monitored at the two locations within the upper layer. Vertical temperature profiles for the two positions within the enclosure were recorded. The furniture calorimeter was operated to provide heat release data for the fires. A series of 12 fires were burned in which the size of the natural gas fires was varied from 40 to 600 kW.

Results

Figure 1 shows time histories of CO, CO_2, and O_2 concentrations at the two sampling positions within the upper layer for a nominal 400 kW natural gas fire in the presence of the wood lining. Time zero corresponds to the ignition of the natural gas. For all of the fires in which wood pyrolysis occurred, it was found that the wood lost its structural integrity and fell from the walls and the ceiling to the floor after a period of time. When the wood fell to the floor, it would generally burn intensely with a bright flame for a short period before settling into a smoldering mode. The vertical lines in Fig. 1 indicate when the collapse of the wood began and was completed. Generally, the wood near the doorway of the enclosure collapsed first, but there was only a short delay before nearly all of the wood had fallen.

The most dramatic effect in Fig. 1 is the rapid growth and peak levels of CO observed before the wood collapsed. Dry CO concentrations reached 7% at the front sampling position and 14% in the rear. Note that oxygen concentrations in the upper layer were very nearly zero during this period as expected. Concentrations of CO_2 were also quite high with the higher levels again found in the rear of the enclosure.

It is significant that following the full collapse of the wood, the CO concentrations in the front and rear of the enclosure fell very rapidly, despite the fact that significant combustion of the wood (as determined by the measured heat release rate) was still occurring. Clearly, the high CO levels are associated with the presence of the wood within the upper layer. The time profiles indicate that the burning wood on the floor significantly disrupted the upper layer (e.g., significant O_2 is observed in the rear of the enclosure immediately following the wood collapse). However, as the wood burning eventually died down, the observed concentrations returned to levels typical of a 400 kW natural gas fire in the absence of wood [11].

High CO levels were generated in all cases where natural gas HRRs were greater than 45 kW. For the smallest fires, an induction period was observed following the start of the natural gas fire before the CO concentration began to increase. Note that fires having HRRs less than 200 kW are overventilated in the absence of wood. The observation of high levels of CO requires that the wood generate sufficient fuel to cause the burning to become underventilated.

Figure 2 compares the time behaviors of CO concentration for two 50 kW fires—one with and one without a wood lining. Only the period from just before the start of the fire until the start of the collapse

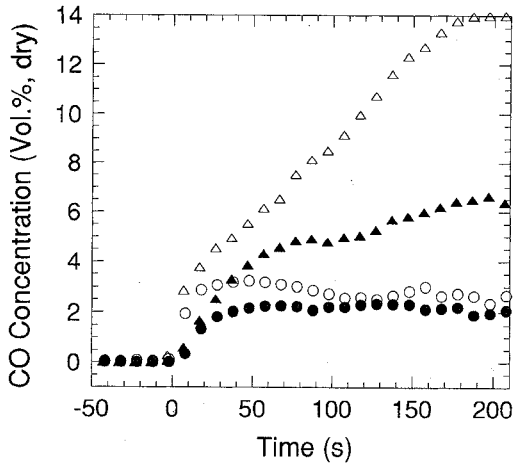

FIG. 3. Volume concentrations (dry) of CO vs time for a 400-kW natural gas fire (○ = rear; ● = front) and for a 400-kW natural gas fire with a plywood lining on the ceiling and upper walls (△ = rear; ▲ = front). The fire was ignited at time = 0 s, and the wood began to fall at 205 s.

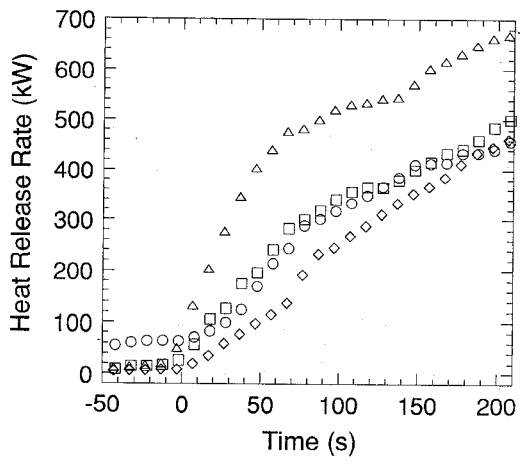

FIG. 4. Heat release rate (kW) vs time for four fires. Each fire was fueled by a plywood lining on the ceiling and upper walls and a natural gas flow corresponding to 50 (○), 100 (◇), 200 (□), or 400 (△) kW. Time zero is defined as the time when the HRR of the fires increased due to the pyrolysis of wood. The wood began to fall at approximately 210 s.

of the wood is shown. The effect of the wood on the observed CO concentrations is obvious, since essentially no CO was detected in the fire without wood. For the wood case, the induction period between the start of the fire and the generation of significant concentrations of CO is apparent.

Similar plots of CO concentration vs time are shown in Fig. 3 for nominally 400 kW natural gas fires. Again, the presence of the wood results in significantly elevated concentrations of CO compared to the fire without a wood lining. Significant CO concentrations are observed in the fire without wood, since this fire is underventilated. Additional CO generated by the wood appears shortly after ignition. Comparison of Figs. 2 and 3 shows that the growth rates of CO concentration with time and the ultimate levels achieved are nearly identical in both cases where wood is present.

Plots of measured HRRs vs time are shown in Fig. 4 for wood-lined enclosure fires in which the heat release rates for the natural gas fires were nominally 50, 100, 200, and 400 kW. It is clear that the wood is contributing significantly to the total HRR of each of these fires.

It is possible to subtract the HRRs for the known flow rates of natural gas from the observed overall values in order to estimate the HRRs due to gases generated by wood pyrolysis as a function of time. If the heat of combustion of the pyrolyzed gases generated by the wood were known, it would now be possible to calculate the mass loss rate of the wood. Unfortunately, the heats of combustion for gases generated from pyrolyzed wood are known to vary, generally increasing with time [22]. Due to the complex nature of the process, these values are also dependent on such experimental parameters as heating rate and pyrolysis temperature [22].

In order to provide an estimate for the mass loss rate, the heat of combustion for a radiatively pyrolyzed sample of the plywood obtained from a Cone Calorimeter [23,24] measurement was utilized. This measurement displayed two distinct temporal regions that are interpreted as corresponding to direct formation of gases by the wood and subsequent pyrolysis of the char that is generated during the direct gasification stage. The average heat of combustion during the gasification stage was 12 MJ/kg, while the pyrolysis of the char stage yielded a much higher value of 25 MJ/kg.

Since the times during which the high concentrations of CO are observed in the current experiments are for the initial wood pyrolysis and the periods are reasonably short, the value of 12 MJ/kg was used to estimate the wood mass loss rate for the period until the wood fell. As a check of the approach, it was assumed that the low HRR applied for the period when the wood was located in the upper layer, and the high value was appropriate after the wood fell. These values, along with estimated HRR data for the wood during the entire burns, allow estimates of the total mass of wood consumed during each burn. The results are within 30% of the initial mass of wood. Figure 5 shows the calculated results for the mass

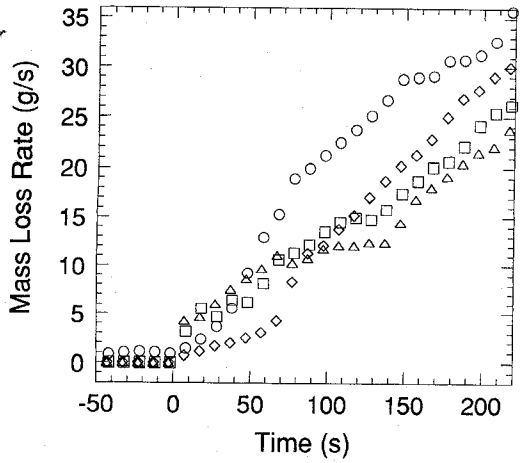

FIG. 5. Mass loss rate of wood (g/s) vs time for the same four fires as in Fig. 4. Each fire was fueled by a plywood lining on the ceiling and upper walls and a natural gas flow corresponding to 50 (○), 100 (◇), 200 (□), or 400 (△) kW. Time zero is defined as the time when the HRR of the fires increased due to the pyrolysis of wood (note the change from earlier figures). The wood began to fall at approximately 210 s.

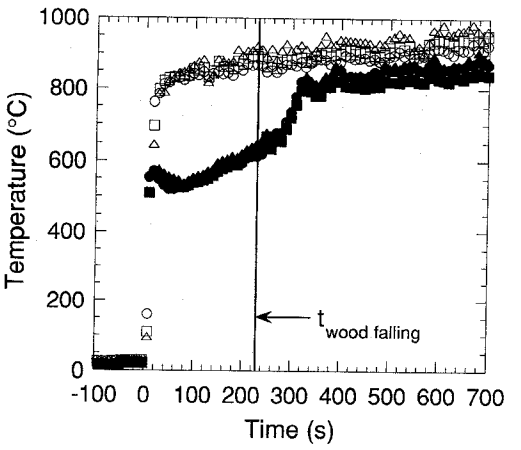

FIG. 6. Temperature vs time for a 360-kW natural gas fire (open symbols) and a 360-kW natural-gas fire with a plywood lining on the ceiling and upper walls (filled symbols). Thermocouples were located 92 cm (○, ●), 88 cm (□, ■), and 84 cm (△, ▲) from the floor. The ceiling is 98 cm from the floor. All of the thermocouples were on the tree located in a front corner of the RSE. The fire was ignited at time = 0 s, and the wood began to fall at 230 s.

loss rate of wood as a function of time over the period before the wood collapses for the 50, 100, 200, and 400 kW natural-gas fires.

A comparison of upper-layer temperature profiles for comparably sized natural gas fires with and without the wood lining allows an assessment of the overall energetics of the wood pyrolysis process for cases when the natural gas fires alone are underventilated. Figure 6 shows temperature-time traces for 360 kW natural gas fires with and without wood at several vertical positions in the front of the enclosure. In the presence of wood, the temperatures are significantly lower. Similar results were found for the other fires having HRRs greater than 200 KW. Assuming that the heat loss mechanisms are not significantly different for the wood-lined and bare enclosures, this requires that the gases generated by the wood pyrolysis cool the combustion gases generated by the natural gas fire, and the overall wood pyrolysis process must, therefore, be endothermic.

Discussion

The hypothesis that the pyrolysis of wood in high-temperature, highly vitiated upper layers results in the generation of very high concentrations of CO is confirmed by the results shown in Figs. 1 through 3. To our knowledge, this is the first demonstration of such a mechanism for the direct formation of CO in enclosure fires. It is likely that this finding provides the explanation for the very high levels of CO observed in the Sharon fire test [13] and for the failure of the GER concept to predict the observed levels of CO.

It is at first glance somewhat surprising that higher concentrations of CO and CO_2 are observed in the rear of the RSE than in the front (Fig. 1). Temperatures in the rear are somewhat cooler than in the front and the wood pyrolysis rate should be slower. The buildup of high concentrations of wood pyrolysis products in the enclosure rear is the result of flow patterns within the enclosure. Gases in the rear of the enclosure have a much longer residence time than the gases flowing out the doorway near the front [12]. As a result, the gases at the front sampling positions are diluted more by gases generated by the natural gas fire plume than the gases in the rear where the gases from the wood pyrolysis accumulate.

The details of the pyrolysis of wood within the RSE are much too complicated to describe in detail. However, the general processes responsible for the generation of gas by wood pyrolysis can be discussed. Here, we adopt the early description of Browne [25].

Pyrolysis is viewed as occurring in four distinct zones:

Zone A (up to 200 °C): Wood is dehydrated and only small amounts of decomposition take place.

Zone B (200–280 °C): A large number of chemical compounds are generated, and charring of the wood begins.

Zone C (280–500 °C): Rapid pyrolysis of wood is initiated, releasing and/or generating a wide range of chemical products, which can undergo secondary reaction, as well as forming charcoal.

Zone D (greater than 500 °C): The surface temperature of the charcoal is sufficient to induce secondary reactions such as

$$C(s) + H_2O(g) \rightarrow CO + H_2 \quad (1)$$

and

$$C(s) + CO_2 \rightarrow 2CO. \quad (2)$$

When the wood in the RSE is exposed to flame gases, it begins to heat from the exposed surface inward. A series of zones develop with the lower-temperature zones moving into the wood and the surface temperature of the wood increasing. If the surface temperature exceeds 500 °C, the fire environment will result in more complicated reactions than simple pyrolysis under inert conditions since significant concentrations of CO_2 and H_2O are present in the flame gases, thus enhancing reactions (1) and (2).

Even though the wood pyrolysis process cannot be studied in detail, it is possible to make checks to see if the results are reasonable. From Fig. 5 and similar results for other fires and using the known surface area of the exposed wood, it is possible to estimate the wood mass loss rate as increasing from 0 to approximately 10 gs^{-1} m^{-2} during the periods before the wood collapsed. The maximum levels are comparable to observed mass loss rates (10–15 gs^{-1} m^{-2}) for samples of the plywood subjected to 50 and 75 kW/m^2 levels of infrared radiation in the cone calorimeter during the period that direct vaporization was occurring. The measured mass loss rate of the wood in the enclosure is consistent with strong heating of a wood sample.

It is not possible to determine the chemical composition of the gases generated by the wood pyrolysis. However, it is clear that large amounts of CO and CO_2 are produced. As a consistency check, it has been assumed that pyrolysis of wood generates only CO, CO_2, and H_2, and the mass production rates have been computed on a global basis using data such as shown in Fig. 5 for the wood mass loss rate as a function of time. Since the flow rates of the natural gas and production rates of CO and CO_2 can be estimated for the natural gas component of the fuel, it is possible to estimate the overall composition of the upper layer by assuming a $CO:CO_2$ mass generation ratio for the wood pyrolysis. Such calculations yield predictions for the observed $CO:CO_2$ concentrations in the front of the enclosure that are consistent with experimental observations. The required $CO:CO_2$ ratio is on the order of 1:1. Based on the ratios for the generation of CO and CO_2 observed for pyrolysis of small particles of wood (see the discussion in the Introduction), this suggests that the average surface temperature for the wood pyrolysis is on the order of 600 °C. The estimated temperature of the pyrolyzing wood surface is considerably lower than the upper-layer gas temperatures (see Fig. 6). This is not too surprising since there are at least two heat loss mechanisms. The wood surface is cooled by heat conduction to the interior, and it has been found experimentally that the wood pyrolysis is overall endothermic, thus requiring heat absorption to proceed.

Final Remarks

The major findings of this study are

1. The pyrolysis of wood in a highly vitiated, high-temperature environment can lead to the production of very high concentrations of CO in enclosure fires.
2. The overall wood pyrolysis is endothermic for the experimental conditions studied.
3. The maximum mass loss rate of wood under the experimental conditions is on the order of 10 gs^{-1} m^{-2}, with the majority of carbon being converted to roughly a 1:1 mixture of CO and CO_2.

These findings have important implications for understanding smoke inhalation deaths that occur in fires. As noted, the conclusions explain the high concentrations of CO generated by the Sharon fire test [13]—a recreation of a fire where CO was known to be responsible for the death of one of the victims. Fire investigations by NIST researchers have provided anecdotal evidence that the generation of CO by wood pyrolysis under conditions similar to those tested for this study is important in numerous multideath fires. Recent examples include the Happyland Social Club fire in the Bronx, NY, which killed 87 persons in 1990 [26], and the Johnson City, TN nursing home fire, which killed 16 people in 1989 [27]. The New York fire resulted from an arson in which gasoline was poured and ignited within a small entryway room lined with plywood and having a fiberboard ceiling. These conditions are very similar to those studied here and would be expected to generate very high concentrations of CO. Most of the fire victims were on the second floor of the building and died as the result of smoke inhalation. The Tennessee fire occurred on the first floor of a multistory building. Victims were found scattered over several floors with the highest being the tenth. Most deaths were again attributed to smoke inhalation. Investigation showed that there was a hidden ceiling above the fire, which consisted of wood fiber tiles attached to wood furring strips and framing members. During the fire, flames broke through the false ceiling and entered air spaces adjacent to the false ceiling. Again, this is a situation similar to the current experiments.

Very high concentrations of CO should have been generated, consistent with casualties far from the fire source.

Additional studies are clearly needed. For instance, it is necessary to determine the conditions for which CO generated within a compartment can exit and be transported without additional reaction. However, as an improved understanding of the conditions responsible for generating dangerous concentrations of CO is obtained, it should be possible to develop predictive methods and strategies for mitigating its effects.

Acknowledgment

The authors would like to thank Dr. Tom Ohlemiller of BFRL for many helpful discussions and for a careful reading of this manuscript.

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COMMENT

Carlos Fernandez-Pello, University of California, Berkeley, USA. Is there experimental evidence of CO production during the pyrolysis of wood in an inert atmosphere such as nitrogen (in a TGA analysis, for example).

Author's Reply. References 14 through 16 describe studies in which wood or related materials were rapidly heated in inert atmospheres to temperatures characteristic of upper layers in underventilated enclosure fires. In each case,

a large fraction of the pyrolyzed material appeared as carbon monoxide for temperatures greater than 900 K. Only one study was identified in which thermogravimetric analysis of wood under inert gases at these temperatures was employed with chemical analysis of pyrolysis products. Hileman et al. [1] found that a Douglas fir sample pyrolyzed at 823 K in helium gave a yield of 21% of its mass as CO. The observed $CO:CO_2$ ratio was 3.7:1.

REFERENCE

1. Hileman, F. D., Wojcik, L. H., Futrell, J. H., and Einhorn, I. N., in *Thermal Uses and Properties of Carbohydrates and Lignins* (F. Shafizadeh, K. V. Sarkanen, and D. A. Tillman, Eds.), Academic Press, New York, 1976, pp. 49–71.