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CARBON MONOXIDE PRODUCTION IN COMPARTMENT FIRES

by

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SUMMARY

The development of empirical correlations for major species yields in compartment fires has become an important priority due to the inability to calculate these quantities from first principles. Studies of simplified upper layer environments have shown that major species production rates can be correlated with the equivalence ratio in what is known as the Global Equivalence Ratio concept (GER). Due to the simplification in these past experiments, it was not known if the GER concept was valid for compartment fires. Therefore, there was a need to determine if correlations existed between major species yields and the equivalence ratio for actual compartment fires.

A 2.2 m^3 test compartment was used to investigate the burning of four fuels (hexane, PMMA, spruce and flexible polyurethane foam) in compartment fires. The test compartment was specially designed with a two-ventilation path system which allowed the direct measurement of the plume equivalence ratio (the ratio of the fuel volatilization rate to the air entrainment rate normalized by the stoichiometric fuel-to-air ratio).

Empirical correlations between the upper layer yield of major species and the plume equivalence ratio were shown to exist. The results reveal that the production of CO is primarily dependent on the compartment flow dynamics (i.e., the equivalence ratio) and upper layer temperature. The correlations developed in the compartment fires are qualitatively similar to those developed by Beyler for simplified upper layer environments. However, quantitative differences exist and can be explained in terms of temperature differences in experiments.

INTRODUCTION

As most fire fatalities are the result of exposure to toxic products of combustion, it is essential that methods be devised to evaluate the toxic hazards posed by specific materials in varying building designs. The primary species of interest is carbon monoxide since studies have shown that over half of fire fatalities are a result of carbon monoxide inhalation[1,2]. Currently, computer codes that model compartment fires lack detailed chemistry and, thus, are unable to accurately predict species concentrations. Equilibrium thermodynamics has also been shown to be inadequate at predicting species concentrations in compartment fires[3].

Since it is not possible to calculate species concentrations in compartment fires from first principles, experimental correlations need to be developed between species yields (grams of species produced per gram of fuel burned) and other measurable parameters. Previous work in hood experiments performed separately by Beyler[4,5], Toner[3] and Morehart[6] has shown that species yields are well correlated to the fuel-to-air ratio. The experiments performed consisted of collecting fire exhaust gases in a hood situated above a burner. Within the hood, a hot layer of combustion products was created, similar to the

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upper layer in a typical compartment fire. Tewarson has also shown that species yields from wood crib compartment fires are correlated to the air-to-fuel ratio[7]. However, the quality of Tewarson's correlations may be compromised by the fact that the air entrainment rate was not measured directly, but rather was calculated from the ventilation parameter, $Ah^{1/2}$, where A is the cross sectional area and h is the height of the vent.

The hood experiments performed by the previous investigators differ from actual compartment fires in several ways. The hood setup allows considerable radiation to the lab space below. Conversely, a real compartment would contain most of the radiation, thus resulting in higher wall and upper layer temperatures. Consequently, higher fuel volatilization rates would be expected for an actual compartment. Also, the hood setup results in a lower layer which has an infinite supply of air which is neither vitiated nor heated. In a real compartment fire, the air supply is limited by the ventilation openings (doors, windows, etc.) and the depth of the upper layer. The air which is entrained into the lower layer of an actual compartment fire can be convectively heated by hot compartment surfaces prior to fire plume entrainment. Lastly, the hood experiments did not include any significant ceiling and wall flame jets. These dynamic flame structures enhance mixing of the upper layer in actual compartment fires and extend the flame zone beyond the plume. Due to the significant differences between the hood experiments and real compartment fires, further work was needed to verify that the correlations observed by Beyler would still hold in more realistic compartment fires.

Ultimately, an optimal correlation would apply for a wide range of fuels and would be robust; that is, a correlation should be independent of all other variables such as vent size, vent aspect ratio, fire size, compartment geometry and the degree of layering. This work was aimed at determining if correlations exist between species generation rates, primarily CO, and the equivalence ratio for realistic compartment fires in which flame jets, reradiation and a limited air supply exist. The results are compared to correlations obtained by Beyler for simplified layer environments. This paper presents observations and quantitative data obtained from burning four fuels in a 2.2 m^3 compartment in which the air entrainment rate and fuel volatilization rate are measured directly by separating the inflow of air and outflow of upper layer gases.

Experimental Apparatus and Procedure

The test compartment, illustrated in Figure 1, was a two-level structure consisting of a 1.2 m x 1.5 m x 1.2 m high fire compartment and a 1.2 m x 1.5 m x 0.37 m high air distribution plenum below this fire chamber. Fire Master 2.54 cm thick fire insulation board (Thermal Ceramics) completely covered the interior surfaces of the fire compartment. A 2.54 cm wide Corning vycor glass window placed vertically down the side of the compartment allowed visual observation of the developing fire. An inlet duct and an exhaust vent provide two ventilation paths in the compartment. Air was naturally drawn into the compartment through a 4 m long, 30.5 cm diameter inlet duct which emptied into the air distribution plenum. The air in the plenum was drawn into the base of the fire compartment through thermally shielded vents on each side of the structure.

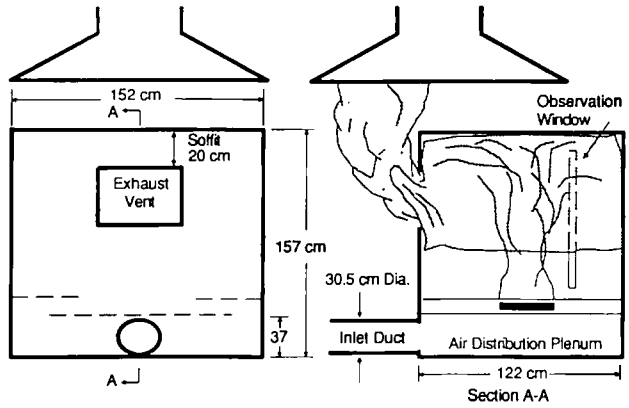

Figure 1. Schematic of the test compartment.

A window style exhaust vent was horizontally centered in the front of the compartment with a 20.3 cm soffit. The vent size was varied to produce different ventilation conditions while also assuring that there was only outflow of combustion products. Exhaust vent sizes ranged from 25.4 cm wide by 15.9 cm high (404 cm^2) to 50.8 x 31.8 cm (635 cm^2). A 1.5 x 1.5 m hood positioned over the exhaust vent collected all fire effluent. The hood was exhausted through a 45.7 cm duct fitted with a gas sampling probe and orifice plate to allow for downstream sampling of the fire effluent and measurement of the volumetric duct flow. A smoke measurement device was situated downstream of the sampling probe and upstream of the orifice plate. The smoke measurement device provided extinction coefficients by measuring the attenuation of a 670 nm laser beam passed through the exhaust duct. From the extinction coefficient, the smoke volume fraction and the smoke yield can be formulated.

The two ventilation path setup allowed direct measurement of the plume equivalence ratio. The plume equivalence ratio, ϕ_p, is the ratio of the fuel volatilization rate to the air entrainment rate normalized by the stoichiometric fuel to air ratio. Most compartment fire work performed to date consisted of compartments with one ventilation path in which both inflow and outflow of gases occurred. Consequently, the entrained air into the compartment can only be estimated from the ventilation parameter $Ah^{1/2}$. The apparatus used for the current investigation allowed the entrained air to be measured directly with the use of a hot film velocity probe (Kurz Inc.) placed in the inlet duct. The velocity probe had a range from 0 to 2 m/s with a an accuracy of ±2.5 percent of the reading. A 15 kg load cell (A&D Inc.), with 1 gram resolution, placed below the fire compartment floor was used to measure the fuel volatilization rate.

The upper layer gas mixture was sampled using an uncooled 0.635 cm stainless steel tube placed 12 cm into the compartment through the center of the exhaust vent. This location for the probe was chosen after species concentration and temperature measurements, taken at several locations in the upper layer, showed a well mixed uniform layer[11].

Measurements consisted of CO, CO_2 and O_2 concentrations, temperatures within the compartment, fuel volatilization rate and air entrainment rate. CO and CO_2 concentrations were measured by Beckman NDIR model 880 analyzers. O_2 concentrations were measured by a Siemens paramagnetic Oxymat SE analyzer. All gas samples were passed through a −10°C cold trap to remove water and a Balston 0.1 micron level filter to remove particulates. Concentrations were compensated for the water removed based on the assumption that the molar ratio of H_2O to CO_2 at any equivalence ratio is equal to the calculated molar ratio at stoichiometric conditions. This assumption leads to an estimated uncertainty in the calculated wet concentration of 1 to 6 percent of the value as the dry CO_2 mole fraction increases from 0.01 to 0.20.

Temperature measurements were made with a vertical tree of eight aspirated thermocouples located in the front corner of the compartment. The thermocouple tree consisted of type K 30 gage thermocouples uniformly spaced 10 cm apart, starting 10 cm from the ceiling. The tree was positioned 10 cm away from the walls to avoid wall jet effects. An unshielded type K thermocouple was also positioned at the sampling probe location.

Four fuels were tested: (1) hexane, (2) cast PMMA, (3) spruce and (4) flexible TDI-based polyurethane foam. The fuels investigated were chosen to provide a varied selection in order to determine if correlations obtained were independent of fuel type. Hexane was chosen as a simple liquid fuel which had been studied previously by Beyler in a hood environment[4]. PMMA was selected as a simple thermoplastic fuel which breaks down almost entirely to its monomer as it volatilizes. TDI-based polyurethane, however, is a more complex polymer that does not decompose to simple monomers. Furthermore, spruce represents a complex cellulosic material that

decomposes directly from a solid to volatiles and char. Besides being complex fuels, polyurethane and wood are also common materials used in building and furnishing materials.

Hexane was burned in 6.4 cm deep circular aluminum pans ranging from 15 to 28 cm in diameter. The PMMA samples burned consisted of 0.95 cm and 1.9 cm thick samples ranging in size from 20 x 20 cm to 46 x 46 cm squares (400 to 2116 cm^2). These sheets were ignited by igniting hexane-soaked PMMA shavings that were evenly piled on top of the sheet to assure a rapid uniform ignition, thus, decreasing the time to steady state burning. Spruce sticks 3.81 cm square, were burned in fuel surface controlled cribs, that is, wide interstick spacing[8]. Crib sizes ranged from 4 to 7 layers and consisted of 3 sticks per layer for 30.5 cm long sticks and 4 sticks per layer for 45.7 cm long sticks. The cribs were placed on aluminum foil pans and ignited with a thin film of hexane poured into the pan. The moisture content of the wood ranged from 11 to 18 percent with an approximate average of 14 percent. The square polyurethane samples were 12.7 cm thick and ranged in size from 30.5 to 45.7 cm on a side. The flexible foam used had a density of 44.1 kg/m^3 and was not fire-treated. Each sample was burned horizontally on the square side and ignited with a propane torch on the top center of the sample. In all cases the fuel was supported by the load cell in the center of the compartment 5 cm above the floor.

Beyler's hood experiments included tests performed with hexane, PMMA and wood. Hexane was burned in a continuously fed, conical surfaced burner such that the area of burning automatically varied to burn the metered fuel supply rate[4]. This burner allowed steady-state burning conditions to be established, whereas in this study, a finite volume of hexane was burned, resulting in more transient fires. Beyler's PMMA slab stock, 2.5 cm thick, was burned with fuel surface areas of 0.023–0.061m^2. Beyler's wood cribs consisted of 3.8 cm thick, 20 cm long ponderosa pine sticks with three to five layers each with three sticks per layer[5].

A quasi-steady-state period was identified for each fire centered about the time at which the equivalence ratio peaked or leveled out. All quantities were averaged over 20 second periods for most fires of hexane and polyurethane and for 60 seconds for most PMMA and underventilated spruce fires depending on the length of the steady-state period. In order to plot the data against the plume equivalence ratio, the stoichiometric fuel-to-air ratio must be defined for each

TABLE 1.
Physiochemical Property Data

FUEL	Volatiles COMPOSITION	$(A/F)_{st}$	k_{co}	k_{co_2}	k_{o_2}
Hexane	C_6H_{14}	0.06579	1.95	3.06	3.53
PMMA	$C_5H_8O_2$	0.1211	1.4	2.20	1.92
Spruce	$CH_{2.473}O_{1.07}$*	0.2119	0.89	1.39	1.10
PU	$CH_{1.74}O_{0.323}N_{0.698}$**	0.1133	1.41	2.21	2.05

$(F/A)_{st}$ = stoichiometric fuel-to-air ratio (mass units)
k_i = maximum yield of species i
PU = 44 kg/m^3 TDI-based polyurethane foam
* assumes 25% char
** does not include nonvolatile filler

fuel. For hexane and PMMA, the stoichiometric fuel-to-air ratio is simply calculated since the elemental composition of the volatiles is readily known. The elemental composition of 44.1 kg/m^3 flexible polyurethane foam was taken to be $CH_{1.74}O_{0.323}N_{0.07}$ [9]. This composition was also verified by an elemental analysis performed by Galbraith labs. A filler accounted for 45 percent of the original weight of the polyurethane and remained as a powder and solid crust after the fire, but had no effect on the composition of volatiles. An elemental analysis, also performed by Galbraith Labs, reported a composition of $CH_{1.689}O_{0.731}$ for the spruce burned. The composition of the volatiles was obtained by adjusting the wood composition for an observed average of 25 percent char; resulting in a volatiles composition of $CH_{2.473}O_{1.07}$. The char was assumed to be all carbon. To calculate the char fraction, the weight of the crib was determined at the time in the fire (after steady-state burning) at which the upper layer O_2 concentration started to rise rapidly, and the CO_2 concentration was also decreasing sharply. The char fraction was then calculated as the weight remaining at this time divided by the initial crib weight. Table 1 shows the physicochemical properties used for the four fuels.

Results and Discussion

Beyler[5], Toner[3] and Morehart[6] separately performed hood experiments that established the existence of distinct correlations between major species yields and equivalence ratios for two-layer fire environments. Two definitions for the equivalence ratio have been used in the literature. Morehart defines an upper layer equivalence ratio as the ratio of the mass of the upper layer that originates from the fuel to the mass of the upper layer that originates from the air stream divided by the stoichiometric fuel-to-air ratio[6]. The plume equivalence ratio, ϕ_p, utilized by Beyler and in this study, is the ratio of the fuel volatilization rate to the air entrainment rate normalized by the stoichiometric fuel to air ratio. As a fire grows, the upper layer composition represents a collective time history of products and, therefore, the upper layer equivalence ratio may lag behind the increasing plume equivalence ratio. However, in a steady-state burning condition, the two equivalence ratios will be equal. Morehart suggests that upper layer species concentrations are insensitive to the plume equivalence ratio but correlate well with the upper layer equivalence ratio[6].

Since finite fuel sources were used in the compartment fires studied, the fires may have been expected to be more transient in nature than the hood experiment fires. In order to determine if the species yield correlations that developed were applicable to transient or steady-state fire environments, the steady-state nature of the fires was investigated by studying the residence time and a steady-state time ratio. The residence time was defined as the time needed for a unit volume of air to move through the upper layer volume. It was calculated by dividing a representative upper layer volume by the inlet air volumetric flow rate, adjusted for the temperature difference between the upper layer and the inlet air duct. Residence times ranged from 3 to 80 seconds. Typically, residence times were 4-10 seconds for hexane and PMMA fires and 15-20 seconds for spruce and polyurethane fires. Beyler's upper layer residence times were on the order of 40 seconds.

A steady-state time ratio was defined as the ratio of the residence time to a characteristic growth time of the fire. Fire growth is directly related to the fuel volatilization rate. Therefore, the ratio of the fuel rate to the derivative of the fuel rate was deemed a representative growth time of the fire. The steady-state time ratios were well below 1.0 for all fires, thereby, signifying quasi-steady-state fire situations. Investigation of individual fires showed that the steady-state ratio decreased below 1.0 at very early times in the fire, thus, indicating that the fires were of a quasi-steady-state nature almost from the start. The assumption is therefore made that the plume and upper layer equivalence ratios are equal and com-

parison between the hood experiments and these compartment fires are on an equivalent basis. Toner and Morehart only investigated gaseous fuels which were not investigated in this study and, therefore, direct comparisons are only made with Beyler's results for similarly tested fuels: hexane, PMMA and wood.

The window placed in the side of the compartment allowed visual observation of the layer interface inside the compartment. For all fuels, the upper layer quickly formed to a depth below the exhaust vent. The layer interface was characterized by horizontal flow of upper layer gases toward the plume and, although wavy in nature, there appeared to be no mixing between layers except at the plume. The layer interface was generally 2 to 5 cm thick. Visual observation confirmed that a distinct recirculating flow pattern developed in the upper layer due to the buoyant force of the plume and the establishment of the layer interface. For overventilated fires, the fire plumes were smaller and ceiling flame jets were small or nonexistent. Ceiling and wall flame jets were observed for underventilated fires, however, layer burning along the interface only occurred for the hexane fires and possibly for several PMMA fires. The occurrence of layer burning was hard to detect for PMMA fires due to heavy smoke build up on the window. Upon layer burning, the layer interface became thicker and more turbulent as cellular flame zones appeared along the interface. Although layer burning resulted in air being entrained into the upper layer other than at the place of plume penetration, the correlations (presented below) between species yields and plume equivalence ratio still apply.

A set of hexane tests were run to determine the uniformity of the upper layer. Due to the quasi-steady-state nature and relatively short burning time of the fires, it was not possible to sample in various locations in the upper layer during a single test. Therefore, a series of hexane fires with the same initial conditions were burned and the upper layer was sampled in a different location for each test. Species concentration measurements taken in different locations of the compartment for the nearly identical tests showed that the layer was uniformly well-mixed[11].

Temperature measurements taken within the compartment also showed quite uniform temperature profiles in the upper layer. It should be noted that in some instances, temperatures deviated up to 20 percent from top to bottom in the layer. This appeared to occur more so during the transition to underventilated conditions and for the overventilated polyurethane and spruce fires. Typically the more underventilated fires for all fuels had uniform temperature distributions. This is attributed to the larger ceiling and wall jets which enhanced mixing in the upper layer. Typically, the upper layer was characterized by about a 20 K temperature rise from front to back in the compartment. This was due to the fact that the inlet duct was attached to the front of the compartment which created a flow pattern leading to more air entrainment into the front of the fire plume. The plume was observed to be slightly deflected towards the rear of the compartment for all fires.

Temperature profiles also showed that the upper layer formed quickly, within one minute. The upper layer depth varied depending on the fuel and the time into the fire. The layer formed to a depth corresponding to the top of the fuel source in the case of spruce and polyurethane (70 to 100 cm). For PMMA and hexane, typical overventilated layer depths were approximately 54 cm. For underventilated conditions the layer interface descended to a depth that was about 23 cm above the PMMA and hexane fuel surface (i.e., a depth of 86 cm). The fire plume extended into the upper layer for all fires.

Although a uniform two-layer system was developed in both the hood and compartment fire investigations, the fire dynamics were significantly different. Larger fires were burned in the compartment experiments with burning rates on the order of 5 to 10 g/s as compared to 0.5 to 1.5 g/s for Beyler's hood experiments. Theoretical heat release rates

ranged from 27 to 660 kW for the compartment fires and only from 11 to 19 kW for the same fuels burned in the hood experiments.

Although the larger fires are primarily a result of using fuel samples that were twice as large in surface area as those used by Beyler, there is also a temperature dependence on the fuel burning rate. Table 2 presents the upper layer temperature data for this study along with the data from Beyler's hood experiments. The data is presented for two ranges of equivalence ratios for the purpose of comparing the fuels and for comparing the hood and compartment experiments. For each fuel, an average for all underventilated fires is presented and shows that the temperature ranks each fuel in the following order: PMMA > hexane > polyurethane > spruce. The average underventilated upper layer temperatures vary from 13 to 24 percent for the compartment fires, contrary to Beyler's hood experiments in which the temperatures agreed within 5 percent for all fuels. The range between an equivalence ratio of 0.5 and 1.5 is of importance in comparing the yield correlations obtained from Beyler's experiments and this study and is discussed below. Beyler observed average temperatures from about 240 to 620 K below those observed for the compartment fires. Due to the elevated temperatures in the compartment fires, radiant heat transfer to the fuel surface is increased resulting in higher burning rates as noted above. For the compartment fires, upper layer temperatures increased with increasing ϕ_p or overventilated conditions and were relatively constant for underventilated conditions.

TABLE 2.
Average upper layer temperatures (K) for selected ranges of equivalence ratios for both the compartment and Beyler's hood fires. The standard deviation is shown in parentheses.

FUEL	TEMPERATURE (K)	
	$0.5<\phi_p<1.5$	$\phi_p>1$
Hexane	970 (83)	1038 (62)
PMMA	1164 (129)	1165 (126)
Spruce*	815 (51)	890 (0)
Polyurethane#	840 (77)	910 (122)
BEYLER:		
Hexane	556 (34)	529 (25)
PMMA	547 (145)	525 (37)
Pine	574 (36)	537 (37)

* ϕ_p >1 represents only one fire

\# ϕ_p >1 represents only two fires

In addition to significant temperature differences, the compartment fires were observed to have larger ceiling and wall flame jets. More for the underventilated rather than overventilated fires, the plume would impinge on the compartment ceiling and spread radially outward. Wall flame jets, extending nearly to the layer, were observed for some compartment fires. This is contrasted with the hood experiments for which no significant flame jets existed. Layer burning was observed for hexane fires both in the hood and these compartment fires. However, when layer burning occurred in the hood experiments the layer could not be contained, thus, resulting in the inability to measure the air entrainment rate. Therefore, Beyler's yield-equivalence ratio correlations only include data for fires with no layer burning. The correlations identified for the compartment fires, however, do include cases in which layer burning and external burning occurred[14].

The burning dynamics of the four fuels burned in the compartment fires varied significantly. Figures 2 to 5 show typical time histories of the four fuels burning in the compartment. The burning time for the fuels varied depending on over- or underventilated conditions, overventilated taking more time to burn. The relative burning times for the fuels can be seen by comparing Figures 2 to 5. After fuel ignition, layer O_2 concentrations

decreased quickly. In some cases, the data acquisition system was started a second or two late, therefore, O_2 concentrations appear below 21 percent at time zero. It is apparent from Figures 2 and 3 that the hexane and PMMA fires burned slowly at first and, as the temperature of the upper layer increased, reached a quasi-steady-state period toward the end of the fire. Both of these fuels exhibit rapid burnout at the end of the fire as denoted by the sudden rise in O_2 and sudden decrease in CO, CO_2 and the plume equivalence ratio. Wood-fueled fires burned rapidly after ignition, reached a peak, sustained a quasi-steady-state period and slowly burned out. Each polyurethane sample, as seen in Figure 5, burned slowly at first as the fire grew radially outward from the top of the sample. As the fire progressed down the sides of the block, the burning rate increased and reached a quasi-steady-state and then decreased relatively slowly. The decrease in the plume equivalence ratio is due to the burning rate decreasing as the surface area of the polyurethane block diminished during burning.

Figures 6, 7 and 8, respectively, show averaged steady-state CO, CO_2 and O_2 wet upper layer concentrations with respect to equivalence ratio for all fuels. For each species, the plots show the same trends for the different fuels with more scatter occurring at higher equivalence ratios for CO and CO_2.

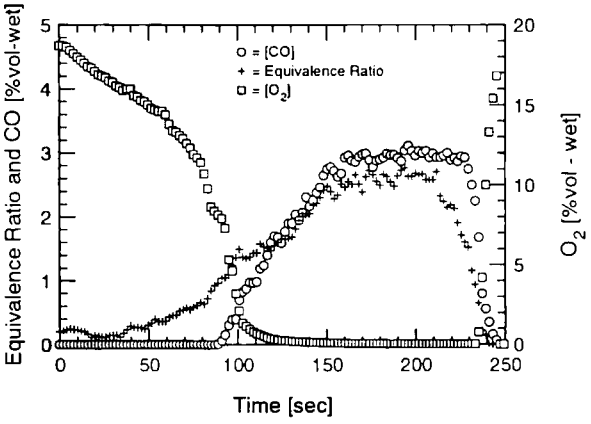

Figure 2 Typical time history of species concentrations and plume equivalence ratio for a hexane fire

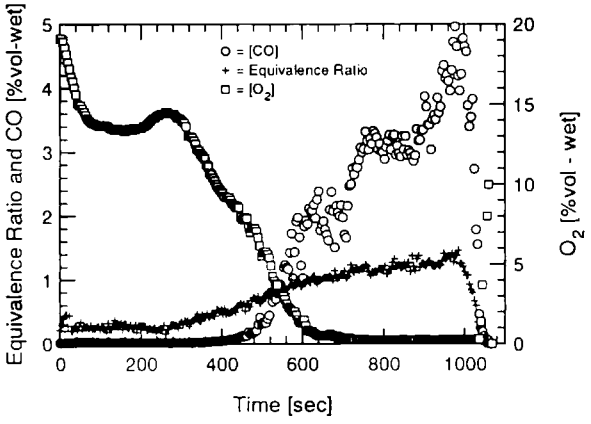

Figure 3. Typical time history of species concentrations and plume equivalence ratio for a PMMA fire

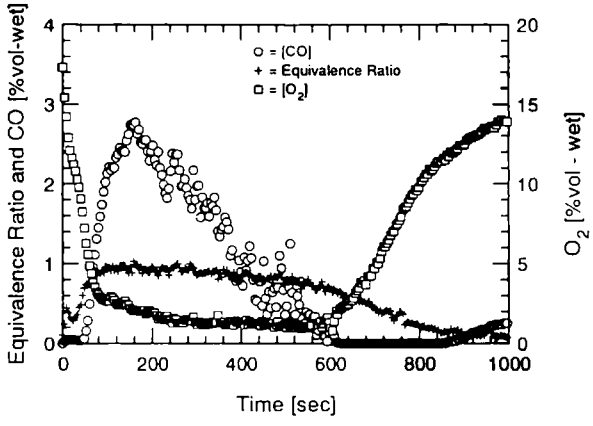

Figure 4 Typical time history of species concentrations and plume equivalence ratio for a spruce fire

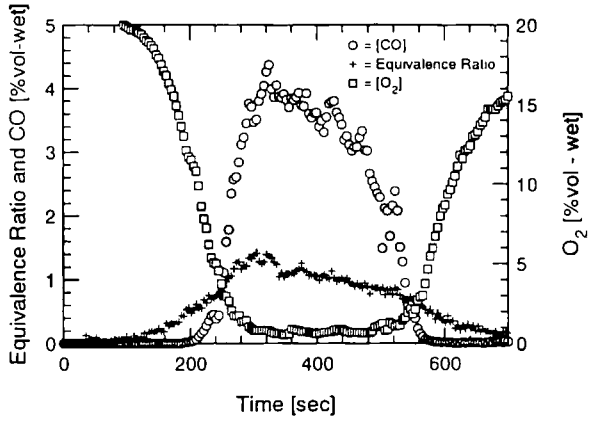

Figure 5 Typical time history of species concentrations and plume equivalence ratio for a polyurethane fire

In general, below an equivalence ratio of one, the CO concentration is below 0.2 percent and the CO_2 concentration is increasing while the O_2 concentration is decreasing with increasing equivalence ratio. Above an equivalence ratio of one, the CO concentration increases, CO_2 decreases slightly and O_2 concentrations approach zero with increasing equivalence ratio. Tewarson reported dry CO concentrations in the same range and up to 9 percent for northern white pine burned in a 2.1 m^3, single opening enclosure[10].

The highest CO concentrations (5.6 and 6.3 percent) were observed for PMMA fires with equivalence ratios of about 1.4. These two fires were for the largest sized samples burned, however, the burning rates were approximately half that of other samples of the same size. As a result, the upper layer temperatures were among the lowest observed (<1050 K) for underventilated PMMA fires. The high concentrations are not fully explained, but are believed to be due to the lower temperature which may cause the fire plume to burn less completely.

Figure 8 shows that for highly underventilated fires, upper layer O_2 concentrations were virtually zero. Tewarson's work also showed near complete consumption of O_2 in underventilated compartment fires[10]. Beyler observed O_2 concentrations that were 1 to 2 volume percent higher than corresponding concentrations for the same fuel and equivalence ratio. He also observed higher CO and lower CO_2 concentrations for hexane and PMMA fires, indicating that the compartment fires burned more efficiently and completely than Beyler's hood fires.

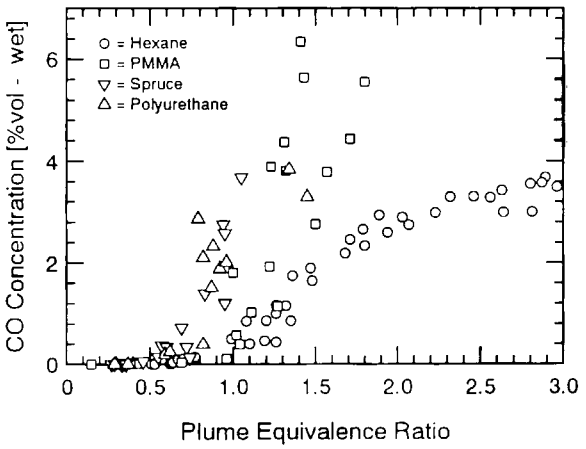

Figure 6 CO concentration versus plume equivalence ratio for all fuels studied

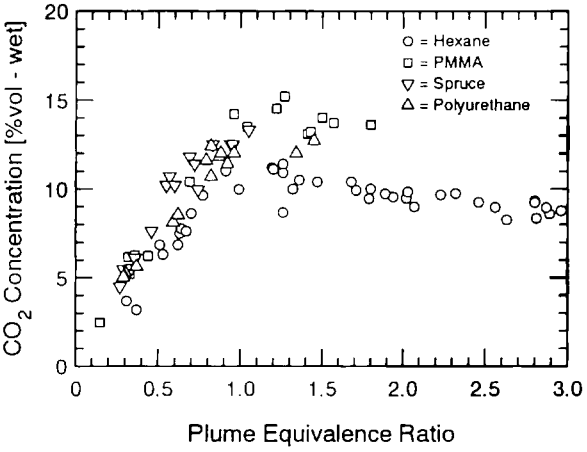

Figure 7 CO_2 concentration versus plume equivalence ratio for all fuels studied

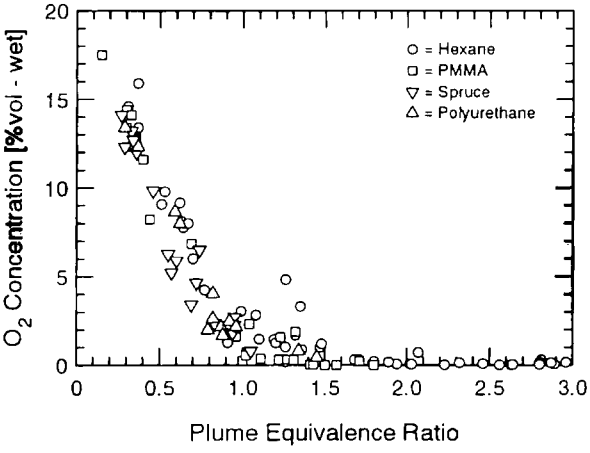

Figure 8 O_2 concentration versus plume equivalence ratio for all fuels studied.

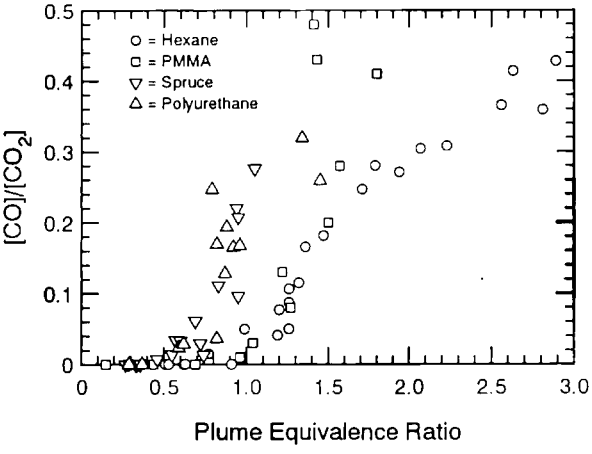

Figure 9. CO/CO_2 concentrations versus plume equivalence ratio for all fuels studied.

The ratio of CO to CO_2 concentrations can be used as an indicator of the combustion mode. High combustion efficiency is obtained the mote a fuel is burned completely to CO_2 and water and is indicated by a ratio of CO to CO_2 near zero. Since CO is a product of incomplete combustion, the ratio of CO to CO_2 concentrations will increase as fires burn less efficiently. Figure 9 shows a plot of the ratio of CO to CO_2 versus equivalence ratio for each fuel. The hexane and PMMA data agree quite well as do the spruce and polyurethane. Values as high as 0.48 for $[CO]/[CO_2]$ were obtained for underventilatedPMMA fires. For hexane and PMMA fires, Beyler observed higher $[CO]/[CO_2]$ ratios for the same equivalence ratio, again indicating that more complete combustion occurred in the compartment fires than in the hood fires.

A useful quantity for fire hazard analysis is the yield of a species. CO and CO_2 yields are defined as the grams of species produced per gram of fuel burned. The yield of O_2 is the grams of O_2 consumed per gram of fuel burned. Figures 10 to 13 show for each fuel the CO yield plotted against the equivalence ratio for both the compartment fire and Beyler's hood experiments. Beyler did not burn polyurethane. The correlations are qualitatively similar, but an offset exists between the rise in CO yield for these tests and Beyler's tests. It is important to note, though, that Beyler's wood data is based on an assumed composition[5]. In contrast, the spruce burned in the compartment fires was analyzed to determine the elemental composition. Since the equivalence ratio is dependent upon the chemical formula in calculating the stoichiometric fuel-to-air ratio,

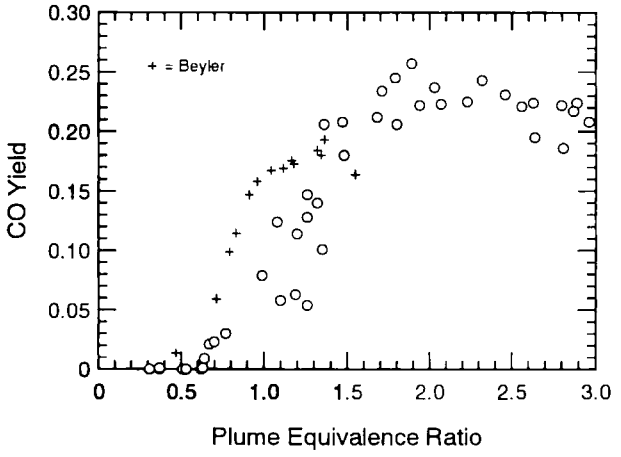

Figure 10. Comparison of CO yield correlations for hexane fires in the compartment and in Beyler's hood

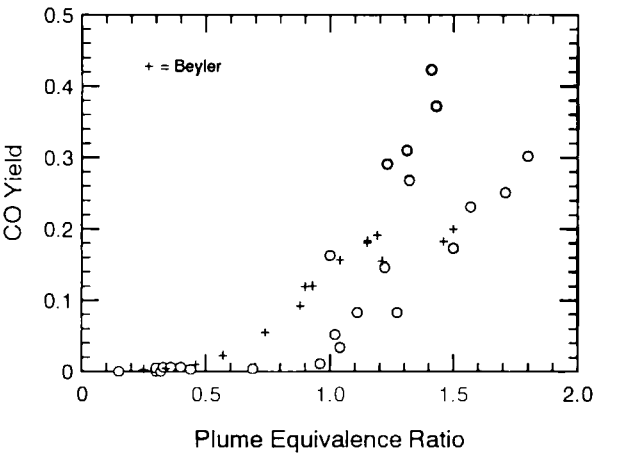

Figure 11 Comparison of CO yield correlations for PMMA fires in the compartment and in Beyler's hood

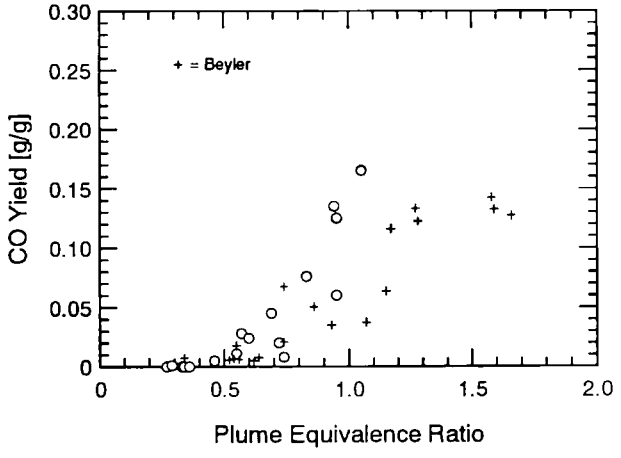

Figure 12. Comparison of CO yield correlations for wood fires in the compartment and in Beyler's hood.

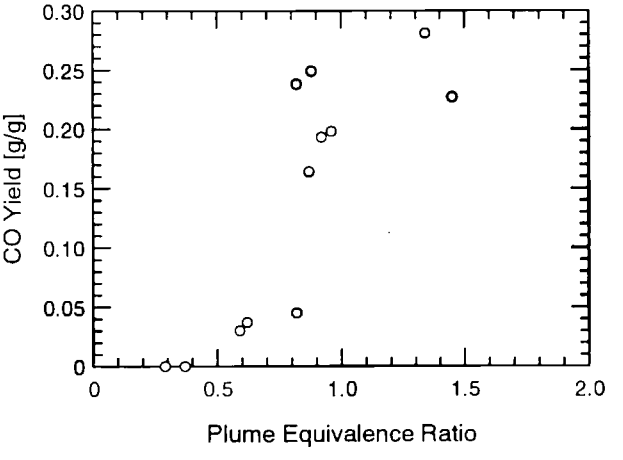

Figure 13. Comparison of CO yield correlations for polyurethane fires in the compartment and in Beyler's hood.

Beyler's correlations may be shifted with respect to the equivalence ratio. Although a qualitative comparison is valid, a direct quantitative comparison between correlations may be suspect.

For the hexane and PMMA compartment fires, CO yields are generally near zero for underventilated fires, as is illustrated in Figure 6 which shows CO concentrations under 2000 ppm for ϕ_p <1. Beyler observed CO yields considerably higher for fires with ϕ_p to about 1.3. Although qualitatively similar, the differences between correlations leadsto asignificantly dufferent hazard assessment for overventilated and slightly underventilated fires. Particularly for hexane fires, CO yields appear to level out for very underventilated fires. The CO yielf approaches a value of 0.18 for the hood fires, and clearly levels out to an average of 0.22 for the compartment hexane fires.

The difference in CO yield correlations is attributed to the temperature difference between experiments. For the primary region of discrepancy between the equivalence ratios of 0.5 and 1.5, Beyler observed average temperatures from about 240 to 620 K below those which were higher than 900 K (see Table 2). The conversion of CO to CO_2 occurs via a reaction with a large temperature dependence. As a result of the lower temperatures in the hood experiments, it is possible for chemical reactions to be quenched in the post-flame (or upper layer) region. Under these conditions of incomplete combustion, higher levels of CO can be obtained. An investigation of this theory can be found in References 11 and 12. The chemical kinetics modeling shows that upper layers with temperatures below 875 K freeze out the conversion of CO to CO_2 in the upper layer. The work also suggests that lower layer temperatures may decrease the temperature of the fire plume resulting in higher CO levels due to incomplete combustion within the plume. The highest temperature observed by Beyler for any fuel was 650 K, which is well below the apparent freeze out temperature.

The CO_2 yield-equivalence ratio correlations obtained for the compartment fires and for Beyler's hood fires are presented in Figures 14 to 17 for each fuel burned. Similarly, the O_2 correlations are presented in Figures 18 to 21. The CO_2 and O_2 yield correlations are qualitatively identical. Up to an equivalence ratio of one, the CO_2 and O_2 yields are fairly constant. Above an equivalence ratio of one, they decrease with increasing equivalence ratio. Both the CO_2 and O_2 yields are dependent upon the fuel composition as would be expected. As the number of moles of carbon in the elemental composition of the fuel increases, there is more CO_2 produced and more O_2 consumed per gram of fuel burned.

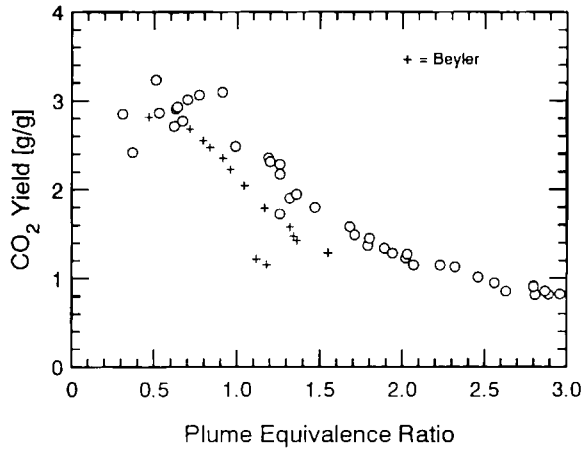

Figure 14. Comparison of CO_2 yield correlations for hexane fires in the compartment and in Beyler's hood

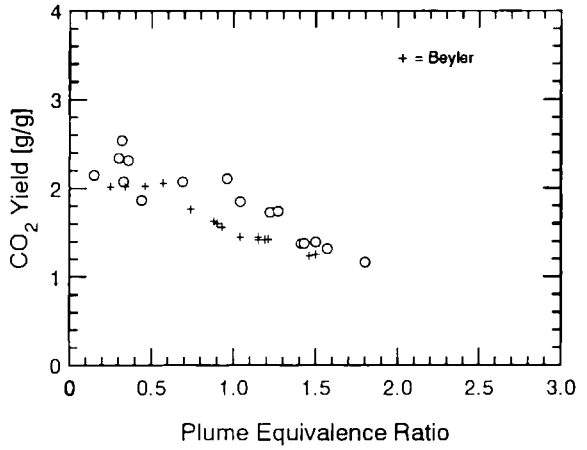

Figure 15. Comparison of CO_2 yield correlations for PMMA fires in the compartment and in Beyler's hood.

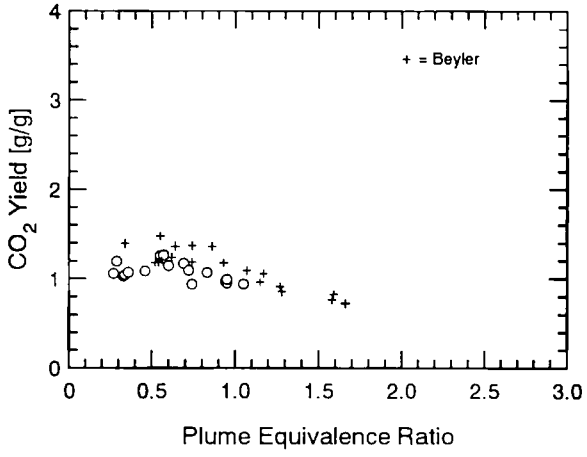

Figure 16. Comparison of CO_2 yield correlations for wood fires in the compartment and in Beyler's hood.

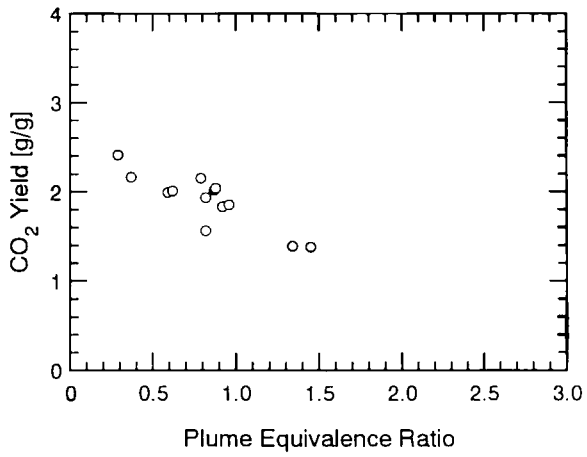

Figure 17 Comparison of CO_2 yield correlations for polyurethane fires in the compartment and in Beyler's hood.

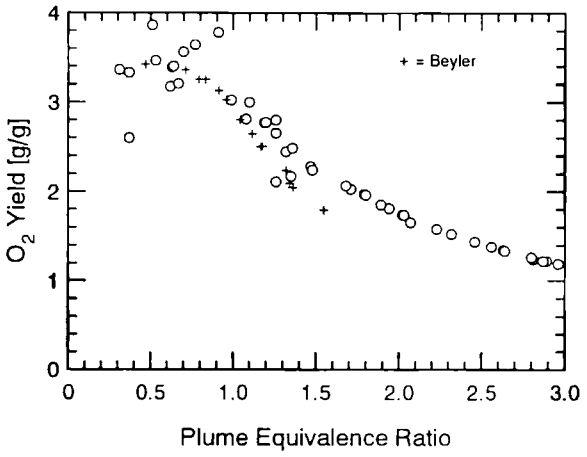

Figure 18 Comparison of O_2 yield correlations for hexane fires in the compartment and in Beyler's hood

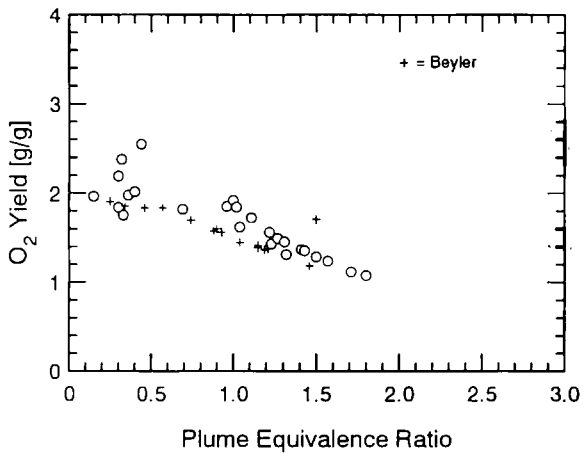

Figure 19 Comparison of O_2 yield correlations for PMMA fires in the compartment and in Beyler's hood.

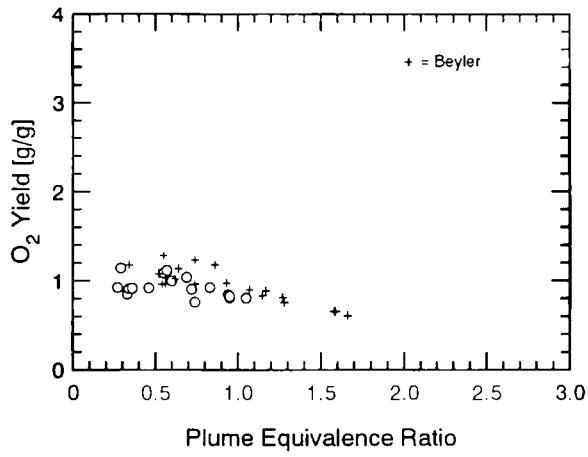

Figure 20. Comparison of O_2 yield correlations for wood fires in the compartment and in Beyler's hood

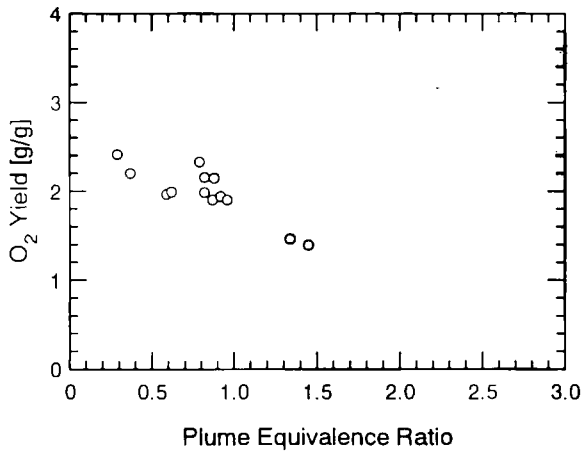

Figure 21. Comparison of O_2 yield correlations for polyurethane fires in the compartment and in Beyler's hood.

Therefore, as can be seen in Figures 14 to 17 and 18 to 21, neither the CO_2 nor O_2 correlations can be represented as a single curve for all fuels.

Beyler's correlations are qualitatively similar to those obtained in this study, however, significant differences exist. Beyler's CO_2 and O_2 yields for hexane and PMMA are lower for underventilated and slightly overventilated fires than the yields observed in this study. The differences between Beyler's CO_2 and O_2 yield correlations can be explained in terms of the shift in the CO yield correlations. If it is assumed that the generation of CO is at the expense of CO_2 and not of total hydrocarbons, then it follows that since Beyler observes higher CO yields for fires with equivalence ratios of about 0.5 to 1.5, one can expect Beyler's CO_2 yields to be less than those for the current work for the same equivalence range. In addition, Beyler observed higher O_2 concentrations, thus indicating that the increased CO observed by Beyler resulted from incomplete conversion of CO to CO_2, rather than a lack of O_2 which would be needed for complete combustion.

So far, it has been shown that yield correlations are qualitatively similar between two-layer environments developed in a hood and developed in a more realistic compartment fire environment. However, substantial differences do exist. Of most importance is the higher CO yields observed by Beyler between plume equivalence ratios of 0.5 and 1.5. The variations between correlations are believed to be explained by layer temperature differences, thus suggesting a need for a temperature correlation.

For the more realistic compartment fires investigated in this study, it is desirable to obtain correlations that are independent of fuel type. Figure 22 shows the CO yield equivalence ratio correlations plotted for all four fuels tested. The primary difference between correlations is that significant CO levels exist for overventilated spruce and

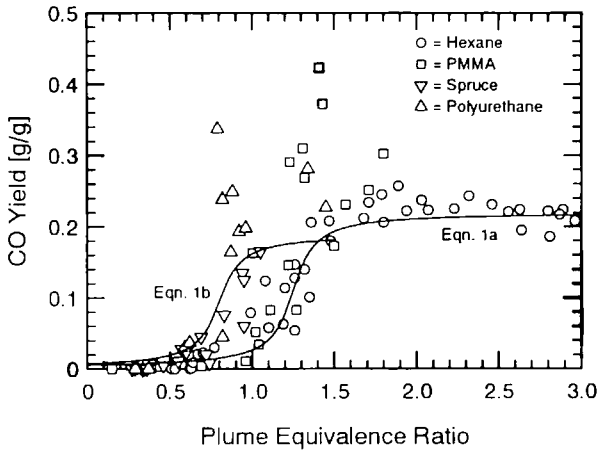

Figure 22 Comparison of CO yield correlations for all fuels tested in the compartment fires.

polyurethane fires but not for the hexane or PMMA fires. The difference is believed to be a result of the upper layer temperature effect discussed above. For the region of interest between ϕ_p of 0.6 and 1, the spruce and polyurethane fires typically had temperatures of 850 K and lower compared to temperatures of 920 K and higher for hexane and PMMA.

Considering that the effect of the layer temperature could be removed and the CO yields appropriately readjusted, the generation of CO, which is a product of incomplete combustion, does not appear to be strongly governed by fuel composition. This is believed to be due to the fact that CO is effectively an "intermediate" product which depends more on the elementary chemistry than on fuel composition which determines products of complete combustion.

Beyler observed that CO yields are higher for fuels with higher oxygen-to-carbon ratios. The hexane and PMMA studied in the compartment fires show the same ranking. This trend is consistent with chemical kinetics modeling which shows that hydrocarbon oxidation is faster than CO oxidation[11,12]. Thus, the oxygenated fuels, which can be considered already partially oxidized, produce more CO faster than the CO can oxidize to CO_2.

As can be seen in Figure 22, the hexane data can be viewed as a lower limit of CO yield observed for all fuels tested. Except for toluene, this is also true for all fuels that Beyler studied. An approximate fit of the hexane data is proposed as a lower boundary of the CO yield in a compartment fire:

$$Y_{CO} = (0.22/180) * \tan^{-1}[10* \phi_p - 1.25)] + 0.11 \quad (1a)$$

where the result of the inverse tangent function is in degrees. This equation is representative of fires with upper layer temperatures greater than 875 K. The effect of temperature on the hexane CO yields is shown in Figure 22 as Equation 1b, which is a fit to Beyler's hood data for hexane fires.

$$Y_{CO} = (0.19/180) * \tan^{-1}[10* \phi_p - 0.8)] + 0.095 \quad (1b)$$

Consistent with the temperature theory, Equation 1b brackets the rise of CO yield at low ϕ_p for spruce and polyurethane burned in the compartment as both had upper layer temperatures below 875 K.

The CO_2 and O_2 yields correlate well with respect to equivalence ratio for each fuel. However, the correlations are quantitatively different and cannot be described by a single curve as can the CO yield data. If the yields are normalized by the maximum possible yield, k_i, of the respective species, i, for each fuel, the correlations collapse down to a single curve for all fuels. Table 1 presents the maximum yields for each fuel.

Normalized steady-state CO, CO_2 and O_2 yields with respect to equivalence ratio are plotted in Figures 23, 24 and 25, respectively. The normalized CO yields correlations for all fuels do not agree as well as the unnormalized yield correlations in Figure 22. A study of Beyler's data reveals the same general conclusions. This is another indicator that CO production is not strongly dependent on fuel type, as is CO_2 and O_2.

For different fuels, the CO_2 and O_2 yield to equivalence ratio correlations only collapse

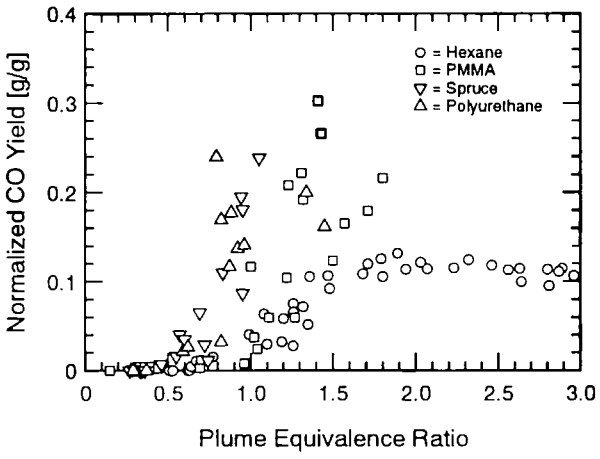

Figure 23. Comparison of normalized CO yield correlations for all fuels tested in the compartment fires.

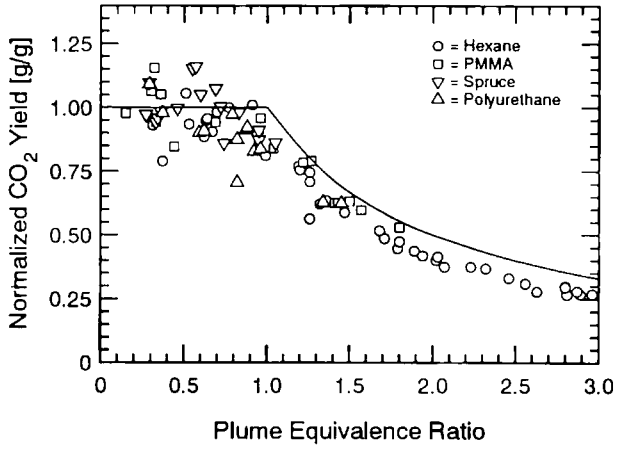

Figure 24. Comparison of normalized CO_2 yield correlations for all fuels tested in the compartment fires.

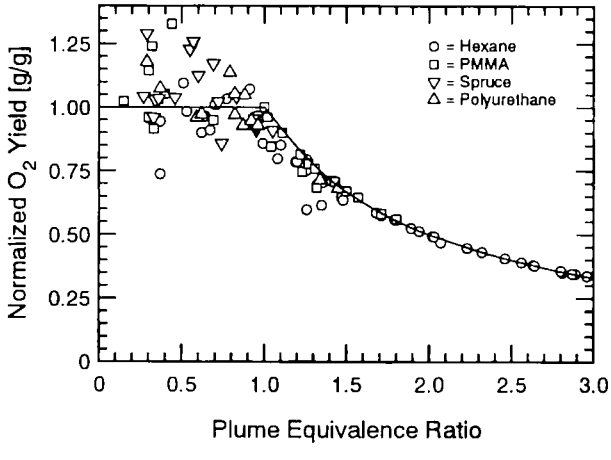

Figure 25. Comparison of normalized O_2 yield correlations for all fuels tested in the compartment fires.

down to a single curve when the yields are normalized by the maximum possible yield for a given fuel. Although complete combustion does not occur, combustion efficiencies are similar enough between fuels that a fuel's particular stoichiometry will dictate the generation of CO_2 and the depletion of O_2. Therefore, the species associated with near complete combustion are not expected to have equal yields for different fuels since varying fuel compositions will dictate different limits of CO_2 that can be generated and O_2 that can be consumed for a gram of fuel burned. By normalizing the yields, the variability of fuel composition is removed.

Figures 24 and 25 show that the normalized yield, f, to equivalence ratio correlations for CO_2 and O_2 agree well between fuel types. Beyler suggests that both correlations can be represented by the following simple model, assuming the most complete combustion of a fuel[5]:

$$f_{CO_2} = f_{O_2} = 1 \quad \text{for} \quad \phi_p < 1 \qquad (2a)$$

$$f_{CO_2} = f_{O_2} = 1/\phi_p \quad \text{for} \quad \phi_p > 1 \qquad (2b)$$

These yield expressions are plotted with the results in Figures 24 and 25. As can be seen, the data agree with the model quite well. The ratio of the normalized yield of CO_2 or O_2 to the predicted values of the model above is defined here as the yield coefficient, B_{CO_2} and B_{O_2}, respectively. These terms are useful in discussing characteristics of the combustion efficiency; for example, an O_2 yield coefficient of 1 indicates complete utilization of available O_2. In the case of CO_2, deviation from the model (as indicated by smaller B_{CO_2}) is a measure of the degree of incomplete combustion. Table 3 shows the average yield coefficients for CO_2 and O_2 for the compartment fires and Beyler's hood fires.

In general, the compartment fires burned more efficiently (i.e,. higher B_{O_2}) and more completely (i.e., higher B_{CO_2}) than the hood fires. As can be seen in Figure 25, nearly complete utilization of O_2 was achieved for the underventilated compartment fires (B_{O_2} > 0.95 on average for all fuels). The deviation of the normalized CO_2 yield for underventilated fires is consistent with the production of CO and unburned hydrocarbons.

TABLE 3.
Average CO_2 and O_2 yield coefficients for all the fuels tested in the compartment fires and for the similar fuels tested by Beyler in hood experiments. The standard deviation is shown in parentheses.

FUEL	B_{CO_2}		B_{O_2}	
	$\phi_p<1$	$\phi_p>1$	$\phi_p<1$	$\phi_p>1$
Hexane	0.93 (0.08)	0.83 (0.05)	0.95 (0.09)	0.96 (0.06)
PMMA	0.99 (0.09)	0.93 (0.04)	1.06 (0.14)	0.98 (0.04)
Spruce*	0.99 (0.09)	0.90 (0)	1.06 (0.13)	0.95 (0)
Polyurethane#	0.90 (0.10)	0.87 (0.04)	1.02 (0.09)	0.97 (0.02)
BEYLER:				
Hexane	0.82 (0.07)	0.61 (0.10)	0.92 (0.04)	0.82 (0.02)
PMMA	0.83 (0.10)	0.77 (0.06)	0.90 (0.07)	0.92 (0.19)
Ponderosa Pine	0.92 (0.08)	0.85 (0.05)	0.93 (0.10)	0.89 (0.03)

* ϕ_p >1 represents only one fire. # ϕ_p >1 represents only two fires.

Tewarson plotted CO, CO_2 and O_2 yields versus mass air-to-fuel stoichiometric fractions (i.e., the reciprocal of the equivalence ratio) for wood crib compartment fires[7]. His results show distinct correlations with good agreement between CO_2 and O_2 data for varied size fires and compartments. The CO_2 and O_2 yields are relatively constant for equivalence ratios up to about 1.7 and 1.4, respectively, and then decrease sharply as the equivalence ratio increases. The CO yield correlates with the equivalence ratio but with a fair amount of scatter in the data. With increasing equivalence ratio, the CO yield increases and, similar to Beyler's correlation for ponderosa pine, appears to be leveling out to a value of about 1.4 for underventilated conditions.

However, the quality of Tewarson's correlations is compromised by the fact that the air entrainment rate used to calculate the mass air-to-fuel ratio was not measured directly, but rather was estimated from the ventilation parameter, $Ah^{1/2}$, where A is the cross sectional area and h is the height of the vent. It is also important to note that the elemental composition of the fuel volatiles used by Tewarson for the wood was not corrected for char yield. A correction of this sort would tend to decrease the calculated equivalence ratio. Although the equivalence ratio data may be suspect, the results are another indication of the validity that clearly defined yield to equivalence ratio correlations exist for realistic compartment fires.

The combustion efficiency, χ_C, is the ratio of the actual heat release rate to the maximum theoretical heat release rate for complete combustion of all fuel (water as vapor). The maximum theoretical heat release rate is simply calculated by multiplying the heat of combustion by the fuel burning rate. The actual heat release rate can be calculated from either the generation rate of CO and CO_2 or the depletion rate of O_2[13]. Due to incomplete combustion and the incomplete utilization of O_2, the O_2 depletion method is not as accurate at underventilated conditions and, therefore, the combustion efficiency data presented here is calculated from CO and CO_2 generation.

Ideal maximum combustion efficiency is unity. However, the maximum possible combustion efficiency is considerably lower for underventilated conditions. For equivalence ratios greater than one, available oxygen becomes the limiting factor of how much fuel can be burned. The maximum possible combustion efficiency, $\chi_{C\,max}$ can be expressed as:

$$\chi_{C\,max} = 1 \quad \text{for } \phi_p < 1 \qquad 3a$$

$$\chi_{C\,max} = 1/\phi_p \quad \text{for } \phi_p > 1 \qquad 3b$$

Figure 26 shows the combustion efficiency plotted against the equivalence ratio for all fuels. The maximum possible heat release rate $\chi_{C\,max}$ is also plotted for comparison. The over- and underventilated average ratio of $\chi_C/\chi_{C\,max}$ is presented along with the average combustion efficiencies in Table 4 for all the fuels tested, including Beyler's data. The correlations for each fuel agree quite well and are well represented by the expression

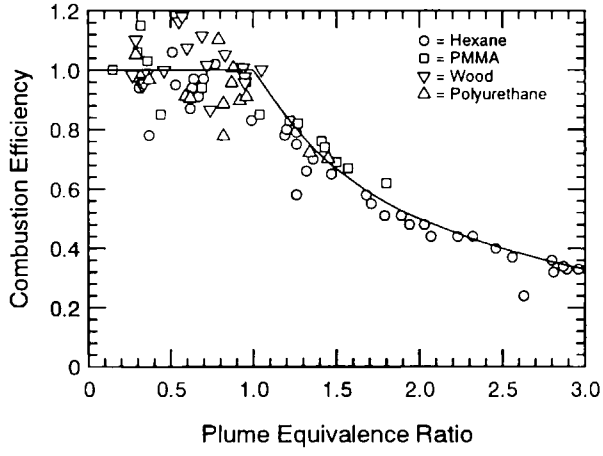

Figure 26. Comparison of combustion efficiency versus equivalence ratio for all fuels tested in the compartment fires.

in Equation 3 for $\chi_{C_{max}}$. The combustion efficiency is relatively constant for overventilated fires and decreases as $1/\phi_p$ with increasing equivalence ratio for underventilated fires. Tewarson reported similar results for wood crib enclosure fires except that quite low combustion efficiencies of about 0.7 for overventilated fires were observed, and the combustion efficiency did not decrease until an equivalence ratio of about 1.4[7]. As discussed above, the equivalence ratio data presented by Tewarson, is suspect. The elemental compositions used for wood studies reported by Tewarson were not corrected for char yield. A correction of this sort would tend to decrease the equivalence ratio and increase the calculated combustion efficiency, more consistent with the compartment fires studied in this work.

Conclusions

Experiments were performed to examine the species production rates for four fuels (hexane, PMMA, spruce and flexible polyurethane foam) burning in a 2.2 m^3 compartment. The compartment was specially designed to separate the entrained air flow from the outflow of upper layer gases. This allowed direct measurement of the entrainedair rate and, thus, the plume equivalence ratio. Therefore, this test facility allowed the study of realistic compartment fire behavior while eliminating the large uncertainty associated with calculating the plume equivalence ratio from the ventilation parameter, $Ah^{1/2}$, as had been done in the past.

Well-defined, empirical correlations between the upper layer yield of major species and the plume equivalence ratio were shown to exist for these compartment fires. The results reveal that the production of CO is strongly dependent on the compartment flow dynamics (i.e., the ratio of the fuel burning rate to the air entrainment rate) and upper layer temperature, and is less sensitive to the fuel type. The production of CO_2 and consumption of O_2 are dependent on theequivalence ratio, temperature and fuel type. However, the production of CO_2 and consumption of O_2 can be represented as normalized yields which removes the fuel type dependence.

TABLE 4.
Average combustion efficiency and average ratio of combustion efficiency to maximum possible efficiency for all the fuels tested in compartment fires and for the similar fuels tested by Beyler.

FUEL	$\chi_{C_{avg}}$		$\chi_C/\chi_{C_{max}}$	
	$\phi_p<1$	$\phi_p>1$	$\phi_p<1$	$\phi_p>1$
Hexane	0.93	0.51	0.93	0.93
PMMA	0.99	0.75	0.99	1.03
Spruce	1.02	1.00	1.02	1.05
Polyurethane	0.94	0.71	0.94	0.99
BEYLER:				
Hexane	0.85	0.54	0.85	0.68
PMMA	0.85	0.68	0.85	0.84
Ponderosa Pine	0.93	0.70	0.93	0.93

The comparison between correlations obtained in the current work and those developed in simplified upper layer environments (Beyler's hood experiments) show qualitatively similar curves. The CO yield and normalized CO_2 and O_2 yield correlations agree quite well for the hexane, PMMA and wood hood fires and the wood and polyurethane compartment fires, as all had upper layer temperatures less than about 875 K. However, the compartment fires with layer temperatures above 875 K, had lower yields of CO and higher yields of CO_2 and O_2 compared to hood fires of the same fuels and equivalence ratios. A chemical kinetics analysis of the upper layer showed that layer temperatures below 875 K freezes out the conversion of CO to CO_2 in the upper layer, resulting in higher levels of products of incomplete combustion.

Since all of Beyler's hood fires had layer temperatures below 650 K, the discrepancies observed between correlations from the hood and compartment fires appear to be mainly due to temperature effects. Therefore, it is concluded that correlations developed in hood apparatus are valid for more realistic compartment fires as long as the effect of layer temperature is considered. The layer temperature dictates post flame oxidation in the layer. Temperatures above 875 K allow nearly complete oxidation of CO to CO_2 for overventilated and slightly underventilated conditions. The correlations developed in this study for hexane and PMMA are examples of the higher temperature effect.

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