The Effect of Oxygen Concentration on CO and Smoke Produced by Flames

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ABSTRACT

A modified cone calorimeter with an enclosure has been developed for measuring the yield of combustion products including CO and smoke under vitiated conditions. The CO yields of methane, propane, PMMA, ABS, polyethylene, and Douglas fir are found to increase by at least a factor of two as the oxygen concentration is decreased from 21% to 14%, while the smoke yields are found to be insensitive to vitiation for the solid materials(less than 30% change). Results for air vitiated separately by nitrogen and by carbon dioxide suggest that the CO yield for a given fuel in a free burn is mainly controlled by the flame temperature. For ambient conditions, the CO yields for the solid samples are about a factor of 2.3 smaller than the smoke yields for all the solid materials studied.

KEYWORDS

carbon monoxide, cone calorimeter, heat release rate, methane, plastics, propane, smoke, vitiation, wood

INTRODUCTION

There have been a number of large scale enclosure fire tests [1,2] in which the CO concentration reached life threatening concentrations of several percent by volume, while the same fuels burning in the open have a much lower yield of CO. Two factors that can affect the CO generation in an enclosure fire are ventilation and vitiation. The ventilation effect comes into play

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when the flow of air into the enclosure is less than the amount required for complete combustion of the vaporized fuel. This leads to a fuel rich combustion with high CO generation. This effect has been studied systematically by Beyler [3] and by Toner et al. [4] by limiting the air entrained into a fire plume. They report large increases in the CO yield for conditions where the equivalence ratio, Φ, defined as the fuel-to-oxygen ratio normalized by the stoichiometric fuel-to-oxygen ratio, exceeds unity.

The second effect, air vitiation, results from the mixing of the fire gases within the burning enclosure and results in a reduced oxygen concentration within the enclosure. Ives et al [5] were apparently the first to conjecture that low oxygen concentration resulted in increased CO production in fires. Their conjecture was based on an extensive review of large scale tests. The present study is directed at providing a quantitative assessment of the effect of vitiation down to the extinction limit on CO yield for methane, propane, and representative solid fuels. To measure the CO yield over the entire range of oxygen concentrations and fuels, it was necessary to measure accurately the CO concentration over the range from 3 to 2000 ppm. While the major focus was on CO yield, we also measured the effect of oxygen concentration of the smoke yield and the burning rate of the fuel. Straightforward correlations for the results are given and comparison is made with the results of other vitiation studies [6,7,8,9].

CONTROLLED ATMOSPHERE CONE CALORIMETER

The standard cone calorimeter (ASTM E 1354 [10], ISO DIS 5660 [11]) has been designed for testing of specimens in ambient air conditions. To explore the effects of oxygen vitiation, CFR/NIST constructed a modified cone calorimeter, wherein the atmosphere being supplied to the combustion zone can be varied. The details of this apparatus including safety features are described in [12]. Figure 1 shows a general view of this controlled-atmosphere cubic-shaped unit with approximately 50 cm sides. A water-cooled shutter is necessary to shield the sample from the radiant heater while the gas concentration perturbation caused by opening the door and inserting the sample dissipates. The combustion air is introduced from the bottom of the chamber and consists of a mixture of compressed shop air and either nitrogen from a 160 L dewar or CO_2 from three 30 kg CO_2 cylinders, each with a commercial heat exchanger to provide an adequate diluent flow up to 4 L/s. The mixed air inflow stream is evenly distributed at a velocity of 3 cm/s as it flows through a glass bead bed. In order to minimize soot deposition on the light extinction optics, the smoke system is sealed on the outside and purged with air. Both inlet and outlet oxygen meters were used and the heat release rate was obtained from the difference in the two readings.

To assure accurate CO concentration measurements at the low CO concentration produced by the burning of some of the fuels, gas calibration standards at 25 ppm and 250 ppm with 1% accuracy were purchased. The resolution of the nondispersive infrared analyzer with gas filter correlation was about ± 0.5 ppm and the typical drift over ten minutes, the nominal test time, was 1 to 2 ppm. Another important feature of the CO analyzer was its wide dynamic range, since the CO concentrations during our tests varied from 3 to 2000 ppm. There is a slight negative cross-sensitivity of the CO meter to CO_2 such that the presence of CO_2 causes a reduction in the CO reading; for example, a 10% CO_2 concentration causes a decrease in the CO reading by

22 ppm. This correction became significant for the gas burner results with CO_2 as the diluent.
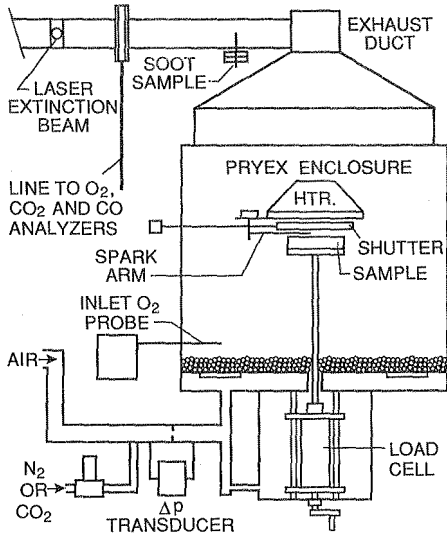

Figure 1. Schematic of modified cone calorimeter designed for controlled atmosphere burning.

The CO yield, Y(CO), defined as the mass of CO produced per mass of fuel consumed, is computed from the total CO generated and the sample mass loss during the active combustion. To obtain accurate values for Y(CO), the inlet and outlet orifice flowmeters were calibrated to an accuracy of ±3% at a flow rate of about 8 L/s, leakage from the enclosure was minimized to less than 5%, and the load cell was isolated from vibrations from the fan and from electrical interference from the igniter.

The smoke yield, Y(S), is computed from the amount of particulate collected on a filter (Pallflex[4] 47 mm diameter fiber glass filter coat with polytetrofluoroethylene), from the mass loss of the sample, and from the ratio of the mass flow through the exhaust duct to the mass flow rate through the filter. From the light transmission measurement through the duct, the specific optical extinction area on a fuel-pyrolysates basis is computed as follows [13]:

$$\sigma_f = k/(\dot{m}_f/\dot{V}),\tag{1}$$

where k is the extinction coefficient per meter, $\dot{m}_f$ is the mass loss rate of the fuel, and $\dot{V}$ is the volumetric flow rate through the exhaust duct.

EXPERIMENTAL PROCEDURE AND RESULTS

The fuels burned included methane, propane, polymethylmethacrylate (PMMA) with carbon additive, acrylonitrile-butadiene-styrene (ABS, high impact resistant), polyethylene-surlyn (ethylene-methacrylic copolymer with zinc ionomer) blend with fiberglass and carbon black additives (PE), and Douglas fir. Wood was chosen because it is the major combustible material present in buildings, PMMA because it is the most widely studied polymer with the cone calorimeter, and the other polymer samples were chosen to provide a diversity of chemical structures. All the solid samples were 10 cm x

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[4] Certain commercial equipment, instruments, and materials 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 for the purpose.

10 cm. The PMMA and PE samples were 6 mm thick (1/4 inch) and weighed about 72 g and 65 g, respectively. The ABS and wood samples were 13 mm thick (1/2 inch) and weighed about 140 g and 75 g, respectively.

The methane and propane experiments involved a 10 cm x 10 cm burner with a 1 cm layer of ceramic fiber blanket to produce a uniform flow. The fuel flow rate was set to give a heat release rate of about 2 kW (0.040 g/s for methane and 0.045 g/s for propane) and the air flow rate set to about 7.5 g/s, which corresponds to about 10 times the air flow required for stoichiometric combustion. The air flow rate was kept constant as nitrogen or CO_2 was added to reduce the oxygen concentration. This procedure maintains a constant global equivalence ratio as the oxygen concentration is varied. As the nitrogen flow is increased the flame becomes more blue in color and the yield of CO increases. As the extinction limit is approached, the flame breaks up into several small flamelets, which move about on the burner surface. For methane the CO yield increases by about a factor of 30 from $6x10^{-3}$ (4-5 ppm concentration) to $1.5x10^{-1}$ (Figure 2) as the nitrogen flow is increased to the extinction limit (14.9% oxygen). When a smaller burner (2.5 cm x 2.5 cm) was used for the same fuel flow rate, similar results were obtained with decreasing oxygen concentration, though the flame lifted off at a oxygen concentration of 16.8% oxygen and extinguished at a concentration of 16.6%. The CO yield for propane, $2.5x10^{-2}$ (about 20 ppm concentration), is about a factor of four greater than for methane at ambient conditions and remains relatively constant until the extinction limit is approached (Figure 2).
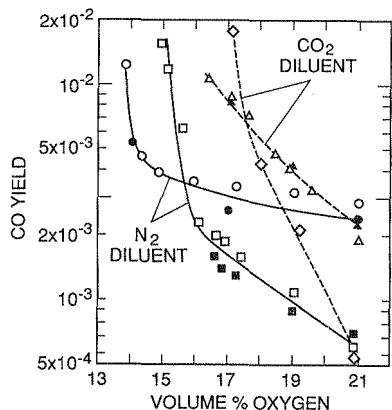

Figure 2. CO yield for methane versus % O_2 with N_2 ($\square$, 10 cm burner; $\blacksquare$, 2.5 cm burner) and CO_2 ($\diamondsuit$) as diluents and for propane with N_2 ($\bigcirc$,$\bullet$) and CO_2 ($\triangle$,$\blacktriangle$).

When CO_2 is used as the diluent gas of the air, the CO yield for both fuels increases more rapidly with decreasing oxygen concentration than when N_2 is used. The CO yield at the extinction limit appears to be insensitive to whether the diluting gas is N_2 or CO_2.

The solid samples were exposed to a radiant flux near the minimum required for spark ignition in order to maintain a low equivalence ratio. In addition, since the air flow rate was held constant as N_2 was added the equivalence ratio was relatively constant as the oxygen concentration was varied for each fuel. The sample mass, gas concentrations of oxygen, CO, CO_2, H_2O, and total hydrocarbon, light extinction of He-Ne laser, and inlet and outlet flows are recorded every 3 seconds for the duration of the test. The filter collection is initiated when the entire sample is actively flaming and then is stopped at the end of active flaming. Repeat tests were performed for each set of experimental conditions. The minimum oxygen concentration for each fuel was selected based on a preliminary test in which a fuel was burned with the oxygen concentration varied until its extinction point was reached. Flame extinction occurred shortly after ignition during several tests, and the tests were repeated at a slightly higher oxygen concentration. The minimum oxygen concentration

required for complete burning of the material, that is, burning to a small residue or char, is underlined in Table 1.

The PMMA formed a liquid film and then ignited in about 70 seconds for a radiant flux of 30 kW/m^2. The PMMA samples burned essentially to completion at all oxygen concentrations forming a slightly expanded surface at the later stage of burning. While the heat release rate increases during the test (Fig. 3a), the heat of combustion and the product yields for CO, CO_2, and H_2O are constant throughout the test. The measured heat of combustion for two tests at ambient O_2 concentration were 26.2 and 26.3 kJ/g, which are about 5% larger than the complete heat of combustion for PMMA. The uncertainty in the determination of the change in the O_2 concentration from inlet to outlet is thought to be the cause of the 5% discrepancy. The average heat release rate decreased about a factor of two from 6.5 kW to 3.7 kW as the oxygen concentration was decreased from 21% to 14% as shown in Figure 3a and Table 1. Over the same oxygen concentration range, the average CO yield increases from 0.005 to 0.013 (Figure 3b) while the specific extinction area of the smoke decreases from about 0.09 m^2/g to about 0.06 m^2/g (Table 1). At a radiant flux of 15 kW/m^2, the increase in the CO yield with decreasing oxygen concentration was less than at 30 kW/m^2 (Table 1). The lower radiant flux results in a smaller mass loss rate and, in turn, a smaller equivalence ratio as indicated in Table 1.
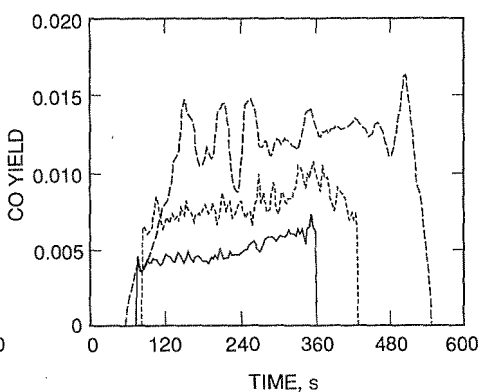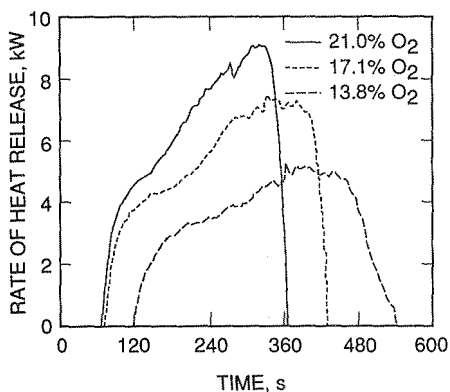

Figure 3a. Effect of % O_2 on the heat release rate for PMMA exposed to 30 kW/m^2 radiation.

Figure 3b. Effect of % O_2 on CO yield.

For ABS both the CO and smoke yields (0.12 and 0.16, respectively at 14% oxygen) are the highest of all the fuels studied. The ABS swells as it burns and produces large soot agglomerates up to several mm in length at ambient oxygen conditions. These large agglomerates did not seem to be present for the reduced oxygen concentration studies. The PE ignited after developing a surface crack. Apparently the fiberglass additive caused the crack to form, since PE without additives does not crack. As the oxygen concentration was decreased, a blue coloration appeared in the lower part of the flame and the sample surface became more visible to the eye. There was at least a hint of this effect for all the solid fuels. For PE, ABS, and

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TABLE 1. CO and Smoke Yield for Solid Fuels[a]

Fuel	Irrad. kW/m^2	O_2 %	$\dot{Q}$ kW	$\dot{m}''$[b] g/m^2s	Y(CO)	Y(CO_2)	Y(S)	σ_f m^2/g	Peak CO ppm	Φ
PMMA	30	21.0	6.5	25	0.005	2.3	0.010	0.09	300	0.29
	30	17.1	5.5	21	0.009	2.2	0.011	0.09	370	0.25
	30	15.1	5.2	19	0.012	2.2	0.008	0.07	390	0.23
	30	13.8[c]	3.7	15	0.013	2.2	0.007	0.06	260	0.16
	15	21.0	5.3	21	0.006	2.2	0.010	0.09	230	0.24
	15	17.1	3.9	15	0.008	2.2	0.009	0.07	240	0.17
	15	16.0	3.4	13	0.010	2.2	0.008	0.08	270	0.15
	15	15.1	3.0	11	0.010	2.2	0.007	0.06	220	0.13
Ref. 14		21.0			0.010	2.1	0.022	0.11		
ABS	30	21.0	6.4	20	0.057	2.4	0.135	1.03	1990	0.29
	30	17.0	5.0	16	0.087	2.3	0.112	0.94	2000	0.22
	30	14.0	2.4	9	0.122	1.9	0.159	0.96	1530	0.11
	20	21.0	5.6	18	0.056	2.4	0.125	0.91	1900	0.25
	20	17.0	4.1	14	0.087	2.3	0.123	0.85	1970	0.18
	20	15.2	2.8	10	0.104	2.0	0.148	0.90	1440	0.12
PE	40	21.0	4.2	10	0.018	2.9	0.048	0.39	330	0.19
	40	17.1	2.8	8	0.028	2.6	0.046	0.35	360	0.13
	40	14.3	3.0	7	0.053	2.7	0.052	0.42	460	0.13
	25	21.0	3.6	8	0.017	2.9	0.039	0.35	240	0.13
	25	17.0	2.6	6	0.025	2.9	0.037	0.31	230	0.12
	25	14.6	1.7	4	0.030	2.9	0.031	0.26	180	0.08
DF	50	21.0	1.4	12	0.004	1.3	0.010	0.08	130,130[d]	0.07
	50	17.0	1.3	12	0.008	1.2	0.009	0.07	160,230	0.06
	50	14.6	1.2	10	0.013	1.2	0.008	0.06	160,190	0.05
	25	21.0	1.4	10	0.004	1.3	0.006	0.05	90,300	0.06
	25	17.2	1.1	9	0.007	1.2	0.003	0.03	80,220	0.05
	25	15.2	1.0	7	0.008	1.4	0.002	0.02	60,200	0.04
Ref. 14		21.0			0.004	1.3		0.04		

[a] The values reported here are averages over the active flaming period. The tabulated results are generally based on duplicate experiments. The reduced oxygen concentrations were obtained by diluting air with nitrogen.
[b] Mass loss rate per unit area.
[c] The minimum oxygen concentrations for complete burning are underlined.
[d] The two values correspond to the two peaks in the CO concentration, one shortly after ignition and the second near the end of the active flaming period.

PMMA the CO yield and specific optical extinction area are relatively constant throughout the burn.

For wood, both the heat release rate and the CO yield have a peak shortly after ignition and a second peak near the end of the test. The enhanced CO yield during the second peak may be due to char oxidation and the high CO yield at the end of the test, which is at least a factor of 10 larger than for the flaming combustion, is characteristic of smoldering wood combustion. In the later stage of wood burning, a small flame may persist while smoldering is also taking place. To avoid this mixed mode result, the yields are computed based only on the active flaming portion of the experiment, during which the flame encompasses the entire sample. Even with this precaution, the results are less consistent for wood than for the other fuels.

The effect of oxygen concentration on CO and smoke yield is summarized in Figure 4a. It is seen that for all the solid fuels the CO yield increases by about a factor of 2.5 as the oxygen concentration is decreased from 21% to 14%. The linearity of the data on a semi-log plot suggests an exponential function to correlate the data. The following expression is consistent with all the CO yield results for the solid samples:

$$Y(CO) = Y^0(CO) \exp(2.7 \, \Delta O_2), \tag{2}$$

where $Y^0(CO)$ is the CO yield at ambient conditions and

$$\Delta O_2 = [\text{Vol.}\%O_2(\text{ambient}) - \text{Vol.}\%O_2(\text{depleted})]/\text{Vol.}\%O_2(\text{ambient}). \tag{3}$$

For _ambient_ conditions, there is a direct correlation between CO yield and smoke yield for all the solid fuels that can be expressed by the relation:

$$Y(S) = (2.3 \pm 0.4) \, Y(CO). \tag{4}$$

The smoke yield is less sensitive to the oxygen concentration than is the CO yield with the yield decreasing slightly with decreasing oxygen for the oxygen-containing fuels, remaining constant for PE, and apparently going through a minimum at 17% oxygen for ABS (Figure 4b).

DISCUSSION

In Table 1 we have also included Tewarson's results [14] regarding CO and smoke yield for PMMA and wood for comparison. The difference in CO yield for PMMA is greater than our estimated uncertainty for CO yield, ± 15%, which includes a 5% random error and a 10% systematic error associated with the CO measurement, flow rate, and load cell measurement. The difference in the CO yields for PMMA may be caused by a factor of 10 higher air velocity in the Tewarson apparatus compared to the cone calorimeter or, perhaps, by a difference in accuracy of the CO concentration measurements. The agreement in the results for wood must be considered fortuitous because of the large uncertainty in the low CO concentration measurement and because of the sensitivity of the measured CO yield to whether the test includes some smoldering combustion.
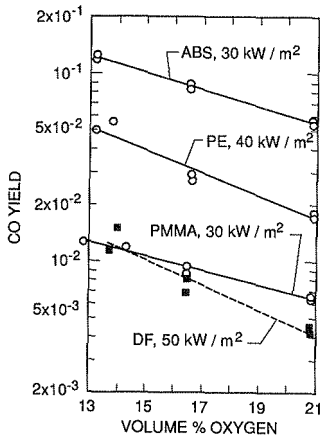
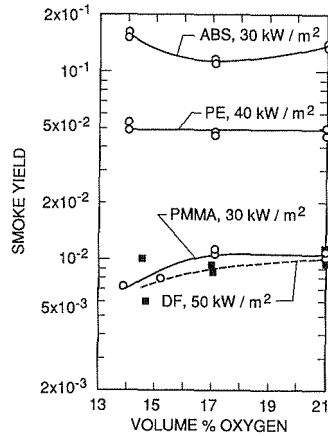Figure 4a. CO yield for solid fuels as a function of % O_2 with N_2 as the diluent.

Figure 4b. Smoke yield for solid fuels as a function of % O_2.

There are a limited number of studies on the effect of oxygen concentration on CO production from fires. The findings of Bromly et al. [6] regarding the effect of air vitiation on the CO/CO_2 ratio for gas appliances is consistent with our study. They find a 30-fold increase in the CO/CO_2 ratio in the exhaust effluent from an unflued sink heater with heat exchanger removed as the heater burned in a sealed room until flame extinction. Our determination of Y(CO) for propane burning in air vitiated to 17.5% with CO_2, 0.007±0.002, is consistent with an estimate of 0.005 to 0.015 based on results by Santo et al. [7] for a 50 kW propane flame burning in air vitiated to 17.5% with CO_2 and H_2O. The Santo result is for the sample collected farthest downstream. For ambient conditions, our value of Y(CO), 0.002 - 0.003, is about half the value reported by Tewarson [14], 0.005.

For the same oxygen concentration, we find that the CO yield is greater when the air is vitiated with CO_2 compared with N_2. The heat capacity of CO_2 is larger than that of N_2, resulting in a lower flame temperature for the CO_2-diluted flame, compared to the N_2-diluted flame for the same oxygen concentration. Computations indicate that the adiabatic flame temperature based on fuel and oxygen meeting in stoichiometric proportions at the lowest oxygen concentration for sustained burning is nearly the same for both diluents (1855 K for N_2 and 1880 K for CO_2, methane; and 1808 K for N_2 and 1856 K for CO_2; propane). This insensitivity of the adiabatic flame temperature at the limiting oxygen concentration to the diluent gas is consistent with calculation made by Egerton and Powling [15]. The CO yields are also similar for both diluents at the limiting oxygen concentration. We conjecture that the CO yield for a given fuel is primarily determined by the flame temperature for free burn conditions ($\Phi < 0.3$). This conjecture would imply that the CO yield in an actual fire environment (N_2, H_2O, and CO_2 vitiating gases) near flame extinction will be similar to the N_2 results near extinction.

While thermodynamic calculations are useful for estimating the effect of the diluent concentration on the flame temperature, they give an incorrect result for the predicted concentration of CO. In fact, the thermodynamic prediction is a decreasing CO yield with decreasing oxygen concentration, contrary to the observed increase. Macek [16] conjectured that at flame extinction all the fuel carbon would be converted to CO. This conjecture was based on the idea that chemical kinetics becomes limiting at extinction where the CO to CO_2 oxidation would be effected by the reduced flame temperature. This conjecture is not correct, at least in terms of the species leaving the flame zone, since the primary carbon-containing gas constituent at extinction is observed to be CO_2 not CO.

For all of the solid samples, a simple correlation was found between CO yield and oxygen concentration indicating at least a doubling in CO yield as the extinction point is approached. A qualitatively similar trend was previously observed by King [9] as he burned thin plastic specimens in the NBS Smoke Density Chamber at ambient oxygen and at 15% oxygen. Also Table 1 from Tewarson and Steciak [8] indicates that Y(CO) for PMMA increases from 0.010 to 0.015 as the O_2 concentration decreased from 22% to 16.5%, though in this case the equivalence ratio is high, 0.7, and ventilation limited effects are also expected.

A direct correlation has been found between smoke yield and CO yield for the solid fuels at ambient conditions. McCaffrey and Harkleroad [17] reported a rough correlation between the light extinction coefficient of the smoke and CO concentration for fires a few hundred kW in size involving propane, crude oil, wood, heptane, and rigid urethane. Tewarson [18] measured smoke and CO yields for 10 plastics; his ratio of smoke yield to CO yield on the average is about 2.5 compared to our result of 2.3. His ratios ranged from about 1.3 to 4, while our range was smaller, 1.9 to 2.7.

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