Smoke Emissions In Fires

ARCHIBALD TEWARSON
FM Global, 1151 Boston-Providence Turnpike, Norwood, MA, 02062, USA

ABSTRACT

Emission of smoke from various fire sizes and fuels has been examined using data from the literature. The data used for the examination were for the fully ventilated combustion of the mixed fuels of all compositions and for non-mixed single hydrogen atom containing fuels, without highly fire-retarded compositions. The combustion data used were for the smaller (0.008 m^2 in area) and larger (0.911-m^2 area) pool-like configuration. The data were also used for the combustion of fuels in vertical wall-like configuration consisting of single panel (0.31-m long and 0.10-m wide) and parallel panels (each panel 2.4-m long and 0.60-m wide separated by 0.30-m and 4.9-m long and 1.1-m wide separated by 0.53-m).

The examination of these data show that the average smoke emission rate, $\dot{G}_S$, depends on the fire size, expressed as the average chemical heat release rate, $\dot{Q}_{ch}$, and the combustion chemistry expressed as the ratio of the yields or emission rates of CO to CO_2 ($y_{CO}/_{CO2}$ or $\dot{G}_{CO}/\dot{G}_{CO2}$ respectively). Correlation is found between $\dot{G}_S$ and $\dot{Q}_{ch}(y_{CO}/y_{CO2})$ or $\dot{Q}_{ch}(\dot{G}_{CO}/\dot{G}_{CO2})$ to the power 0.96 with a correlation constant of 0.053. The correlation limits are in the range of 0.0008 to 8 g/s for $\dot{G}_S$ and 0.015 to 100 kW for $\dot{Q}_{ch}(\dot{G}_{CO}/\dot{G}_{CO2})$. The correlation holds for particulate dominated smoke and for fuels with non-particulate dominated smoke in the presence of H and OH atoms provided by other fuels or by the ignition source, such as a hydrocarbon gas burner. Deviation of the experimental data from the correlation appears to be due to the unaccountability of the non-particulates by the optical technique used to measure the particulates. A new technique that could measure both particulates and non-particulates in smoke would make the correlation to hold for all types of fuels and for all types of fire conditions including ventilation. Such a generalized correlation would be useful for smoke modeling and for the smoke hazard assessment.

KEYWORDS: Fire chemistry, fire modeling, heat release rate, smoke emission, hazard evaluation, fire investigation.
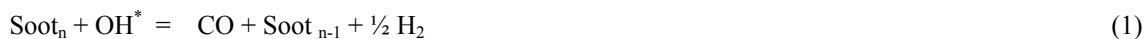
NOMENCLATURE LISTING

f_j	Emission efficiency of a product (y_j/Ψ_j)	*Greek*	
FPA	Fire propagation apparatus	χ	Combustion efficiency
FPC	Fire Products Collector	η	Fraction of particulates and non-particulates
$\dot{G}_j$	Emission rate of a product (g/s)	ξ	Ratio of the emission rates of CO to soot (g/g)
ΔH_{ch}	Chemical heat of combustion) (kJ/g)	Ψ_j	Mass stoichiometric yield of a product (g/g)
ΔH_T	Net heat of complete combustion (kJ/g)	κ	$\Delta H_T / \Psi_{co2}$ (kJ/g)
$\dot{m}_f$	Emission rate of fuel vapors (g/s)	Φ	Equivalence ratio (g/g)
m_j	Mass concentration of a product ($\mu g/cm^2$)	*Subscripts*	
M	Molecular weight (g/mole)	f	Fuel
n	Number of carbon atoms	*np*	Non-particulates
PPT	Parallel panel test	p	Particulates
		s	Smoke
$\dot{Q}_{ch}$	Chemical heat release rate (kW)	*Superscripts*	
X_H	Hydrogen atom mass fraction in the fuel	$\cdot$	Per unit of time (1/s)
y_j	Yield of product j (g/g)		

INTRODUCTION

CO and smoke are products associated with incomplete combustion of a fuel, health problems due to air pollution, fire safety (toxicity and reduced visibility), and property damage in fires (malodor, stain, corrosion, and malfunction of electrical/electronic circuits). CO is a gaseous compound, whereas smoke is a mixture of particulates (mostly soot) and non-particulates consisting of organic compounds [1]: 1) VVOC (very volatile organic compounds): boiling points < 0 to 50-100 °C; 2) VOC (volatile organic compounds): boiling points between 50-100 to 240-260 °C, and 3) SVOC (semi-volatile organic compounds): boiling points between 240-260 to 380-400 °C. Some of the SVOC may behave as particulates.

It is generally accepted that CO and soot compete for free radicals, especially OH and O and thus their formation and emission depend on the availability of free radicals [2-9]. The following overall kinetics for the soot and CO emission has been suggested [2]:

$$Soot_n + OH^* = CO + Soot_{n-1} + \tfrac{1}{2} H_2 \qquad (1)$$

$$Soot_n + \tfrac{1}{2}O_2 = CO + Soot_{n-1} \qquad (2)$$

$$Soot_n + O = CO + Soot_{n-1} \qquad (3)$$

where $Soot_n$ represents a soot particle with n carbon atoms. Such a representation may be fair approximation for soot escaping a flame when the C/H ratio of the particle is large ($\cong 8$).

Fully ventilated combustion data show that CO and soot emissions are correlated and the ratio of their emission rates (or yields) is a constant [2-10]. It is thus suggested that there is a similarity between the kinetic and air-fuel mixing processes that govern the formation and oxidation of both CO and soot [5, 7, 8]. However, the ratio is not a constant and increases for highly charring, highly halogenated and highly fire retarded fuels with negligible or no hydrogen atoms in the structure and for the under-ventilated fires. The influence of charring, fire retardants and absence or negligible amounts of hydrogen atoms in the fuel structure is compensated if these fuels are burned with other hydrogen atom containing fuels. Examples are the larger-scale parallel panel tests where high intensity propane burner is used as the ignition source that provides H and OH atoms [11, 12, 13].

The literature data has been used to establish a correlation between the smoke emission rate and heat release rate (governed by the fire size) and the ratio of the yields or emission rates of CO and CO_2 (governed by the combustion chemistry or the generic nature of the fuels) for the fully ventilated conditions. The literature data used in the paper were measured in the smaller-scale experiments in the Fire Propagation Apparatus (FPA) and in the larger-scale experiments in the 5-MW Fire Products Collector (FPC) at FM Global [6, 10 to 14 and references there in] for the fully ventilated combustion conditions.

RELATIONSHIPS BETWEEN SMOKE EMISSION, FIRE SIZE AND COMBUSTION CHEMISTRY

Heat release rate represents the fire size that can vary by several orders of magnitude between the smaller-scale and larger-scale experiments. The yield or emission rate ratio of CO to CO_2 represents the combustion chemistry, which is affected by the generic nature of the fuel as well as by the fire conditions.

Heat Release Rate, ($\dot{Q}_{ch}$):

$$\dot{Q}_{ch} = \Delta H_{ch}\dot{m}_f = \kappa y_{co2}\dot{m}_f = \chi \Delta H_T \dot{m}_f \qquad (4)$$

where ΔH_{ch} is the chemical heat of combustion (kJ/g) and $\dot{m}_f$ is the emission rate of fuel vapors (g/s), χ is the combustion efficiency, $\kappa \approx \Delta H_T/\Psi_{CO2} \approx 13.3\ g/g$, where ΔH_T is the net heat of complete combustion (kJ/g), y_{co2} is the yield of CO_2 (g/g) and Ψ_{CO2} is the stoichiometric yield of CO_2.

Smoke Emission Rate ($\dot{G}_s$):

$$\dot{G}_s = y_s \dot{m}_f = (y_{co} / \xi) \dot{m}_f \tag{5}$$

where y_s is the yield of smoke (g/g), y_{co} is the yield of CO (g/g) and ξ is the ratio of the yield of CO to the yield of smoke. From Eqs. 4 and 5:

$$\dot{G}_s \approx (1 / \xi\kappa)\dot{Q}_{ch}(y_{CO} / y_{CO2}) \approx (1 / \xi\kappa)\dot{Q}_{ch}(\dot{G}_{CO} / \dot{G}_{CO2}) \approx 0.075\,(1 / \xi)\,\dot{Q}_{ch}(\dot{G}_{CO} / \dot{G}_{CO2}) \tag{6}$$

where $\dot{G}_{CO}$ is the emission rate of CO (g/s) and $\dot{G}_{CO2}$ is the emission rate of CO_2 (g/s). In Eq. 6, ξ and $\dot{G}_{CO} / \dot{G}_{CO2}$ depend on the combustion chemistry that is governed by the fuel structure and fire ventilation conditions, whereas $\dot{Q}_{ch}$ depends not only on the combustion chemistry but also on the fire size. The dependency of these parameters on the combustion chemistry that is governed by the fuel structure and fire ventilation conditions is reflected in the data in Figs. 1 to 3. Note that for a fuel for fixed $\dot{m}_f$ value $\dot{Q}_{ch}$ varies with χ according to Eq. 4 as ΔH_T is a constant for the fuel.

Dependency of the combustion efficiency on fire ventilation (Fig. 1)

For each generic type of fuel, χ remains approximately constant for the fully ventilated conditions ($\Phi \leq 0.70$) and decreases as the conditions change to under-ventilated or fuel-rich ($\Phi > 0.70$). With decrease in χ, combustion becomes less efficient and $\dot{Q}_{ch}$ and $\dot{G}_{CO2}$ decrease and $\dot{G}_{CO}$ and $\dot{G}_S$ increase. The value of χ varies in order of PMMA (aliphatic-oxygenated-hydrocarbon-type) > PE (aliphatic-hydrocarbon-type) > wood (similar to PMMA) > PS (aromatic-hydrocarbon-type) >PVC (halogenated-hydrocarbon type).

Dependency of ξ and $\dot{G}_{CO} / \dot{G}_{CO2}$ on fire ventilation (Figs. 2 and 3)

The dependency of ξ and $\dot{G}_{CO} / \dot{G}_{CO2}$ on the combustion chemistry is opposite to the dependency of χ. This suggests that the inter-relationship between $\dot{G}_S$, ξ, $\dot{Q}_{ch}$ and $\dot{G}_{CO} / \dot{G}_{CO2}$, in Eq. 6 is a complex one.
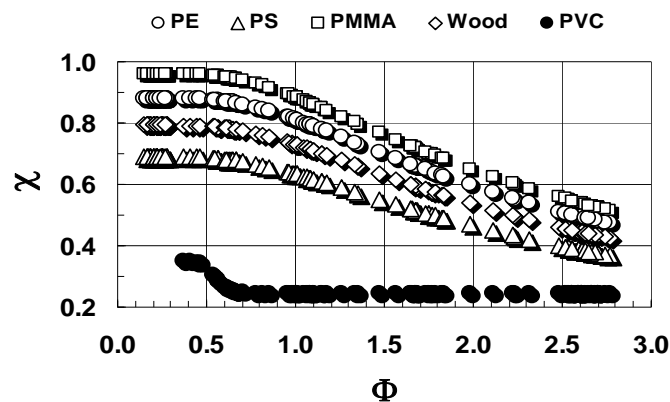

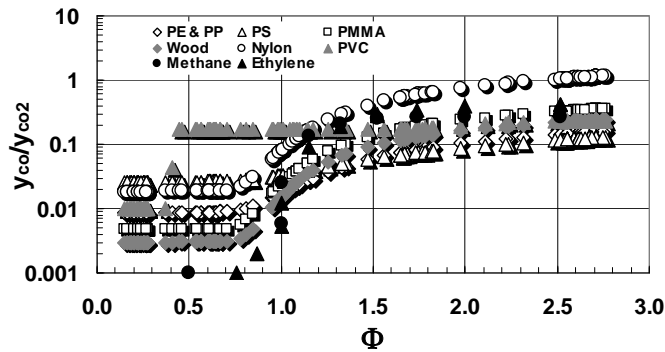Fig 1. Combustion efficiency versus the equivalence ratio. Data are taken from Ref. 6.

Fig 2. Ratio of the yields of CO to CO_2 versus the equivalence ratio. Data are taken from Ref. 5 (methane and ethylene) and Ref. 6.
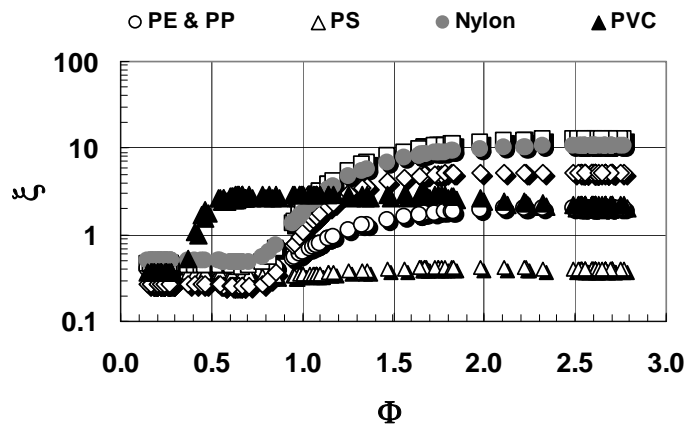

Fig 3. Ratio of the yields of CO to smoke versus the equivalence ratio. Data are taken from Ref. 6.

FUEL CONFIGURATION AND TEST APPARATUS

Data for the combustion of polymers available in the literature were used in this paper. The data were measured in a pool-like and wall-like configurations in smaller- and larger-scale experiments for the fully ventilated conditions [6,10-14 and references there in]. Data for the combustion of polymers in a pool-like configuration were from two sizes of pools: 1) 0.008 m^2 area pool used in the smaller-scale experiments in the Fire Propagation Apparatus (FPA) with external heat flux in the range of 10 to 60 kW/m^2; and 2) 0.90-m^2 pool area used in the larger-scale experiments in the 5-MW Fire Products Collector (FPC) in normal air.

Data for the combustion of polymers in a wall-like configuration are from the three sizes of vertical panels of the polymers: 1) 0.31-m high and 0.10-m wide vertical polymer panel used in the small-scale experiments in the FPA with an external heat flux of 60 kW/m^2 and an oxygen concentration of 40 %; 2) two 2.4-m high and 0.60-m wide panels facing each other, separated by 0.30-m with a 0.60-m long x 0.29-m wide x 0.30-m deep propane sand burner at 60 kW at the bottom between the panels under the 5-MW FPC; and 3) two 4.9-m high and 1.1-m wide panels separated by 0.53-m with a 1.1-m long x 0.50-m wide x 0.30-m deep propane sand burner, set between 60 to 360 kW, at the bottom between the panels under the 5 MW FPC. Figure 4 shows a photograph of a test for PVC panels under the 5-MW FPC.

Fig 4. Two 4.9-m x 1.1-m PVC panels with a heat exposure of 360 kW from a propane burner under the 5-MW FPC. Figure is taken from Ref. 13.

FUELS

Data for the following fuels were selected to represent large variations in the combustion chemistry because of the variations in the generic nature of the fuels:

1. Low smoke emitting polymethylmethacrylate (PMMA: ordinary polymer);
2. Low smoke emitting plywood (wood product);
3. Low smoke emitting chlorinated polyvinylchloride (CPVC: lower hydrogen, highly chlorinated polymer);
4. Low smoke emitting polyvinylidenefluoride (PVDF: lower hydrogen, high temperature fluorinated polymer);
5. Low smoke emitting polyetheretherketone (PEEK: lower hydrogen, high temperature polymer);
6. Low smoke emitting ethylenechlorotrifluoroethylene (ECTFE: low hydrogen, highly halogenated polymer);
7. High smoke emitting polystyrene (PS: aromatic polymer);
8. High smoke emitting polyester wall paneling (commercial product);
9. High smoke emitting polyethersulfone (PES, high temperature polymer);
10. High smoke emitting polyvinylchloride (PVC: ordinary halogenated polymer);
11. Low smoke emitting cables: combination of fluorinated ethylene-propylene (FEP, no hydrogen atom) insulation and jacket and highly fire retarded polyvinyl chloride (PVC) insulation and jacket;
12. High smoke emitting cables: cross-linked polyethylene (XLPE) with and without the fire retardant (FR) as insulation and PVC with and without FR as jacket or chlorosulfonated polyethylene (CSPE) jacket.

DATA ANALYSIS

Correlation between Smoke Emission Rate and Heat Release Rate Times the Ratio of the Emission Rates of CO and CO_2

Equation 6 consists of a combination of $\dot{Q}_{ch}$, ξ and $\dot{G}_{CO}/\dot{G}_{CO2}$ all of which depend on the fire size and combustion chemistry, such as shown in Fig. 5, where data from Figs. 2 and 3 have been used. In Fig. 5, a power relationship is indicated between ξ and y_{CO}/y_{CO2} (or $\dot{G}_{CO}/\dot{G}_{CO2}$), which probably also applies to the relationship between $\dot{Q}_{ch}$, ξ and $\dot{G}_{CO}/\dot{G}_{CO2}$. Thus, a power-type regression analysis was used for the literature data for the fully ventilated combustion to develop a correlation based on Eq. 6, which is shown

in Fig. 6. The correlation is limited to the following ranges: 1) $\dot{G}_S$ from 0.0008 to 8 g/s and 2) $\dot{Q}_{ch}(\dot{G}_{CO}/\dot{G}_{CO2})$ for 0.015 to 100 kW. Data beyond these ranges are mostly for single fuels with little or no hydrogen atoms in the structure, measured in the smaller-scale experiments in the FPA, in the absence of fuels that supply H and OH atoms. Highly charring, highly fire retardant and highly halogenated fuels are examples of these types of fuels. Since the power of 0.96 in Fig. 6 is close to unity, the relationship in Fig. 6 is similar to Eq. 6 and thus the correlation constant 0.053 kJ/g $\approx 0.075/\xi$ that suggests that $\xi \approx 1.42$ g/g.
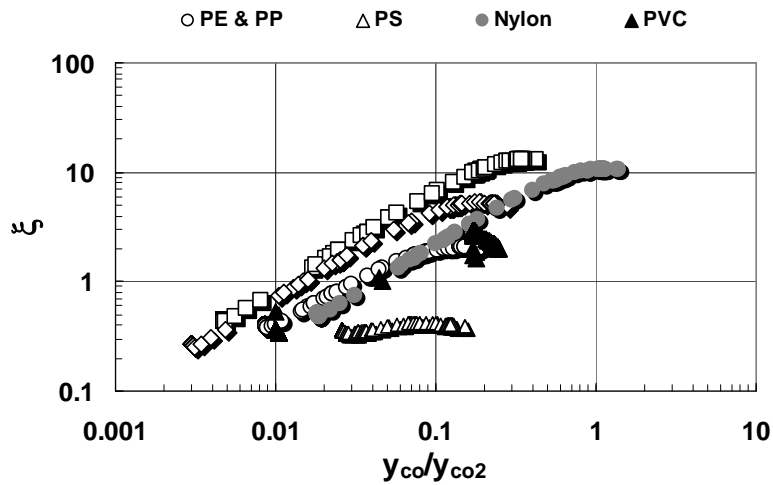

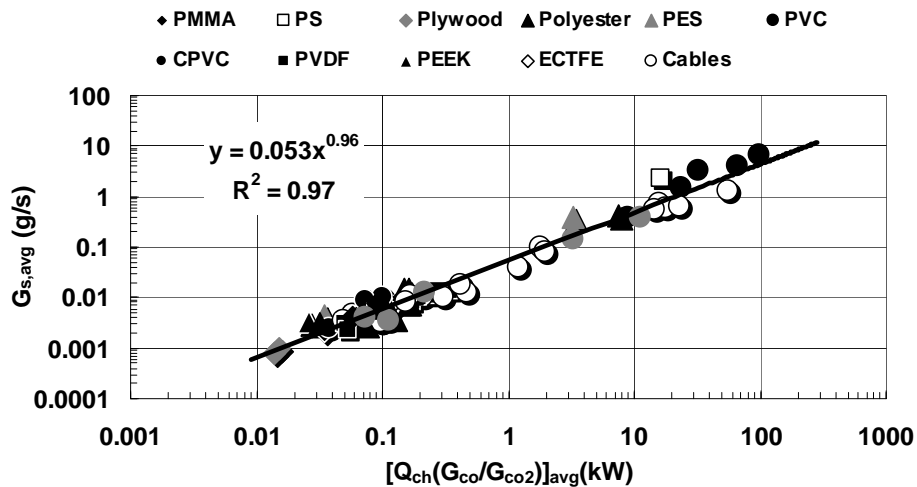Fig 5. Ratio of the yields of CO to smoke versus the ratio of the yields of CO to CO_2

Fig 6. Average smoke emission rate versus the chemical heat release rate times the ratio of the emission rates of CO to CO_2.

Emission Rate Ratio for CO to Smoke (ξ)

The ξ values for some selected fuels are listed in Table 1. For ordinary polymers, gases and liquids, smoke is dominated by the particulates and the average value of $\xi = 0.34 \pm 0.05$ g/g [10 and references therein], showing that larger fraction of fuel carbon is converted to soot than to CO. These fuels have higher number

hydrogen atoms relative to the carbon atoms in the fuel structure and it is suggested that soot is formed via the polycyclic aromatic hydrocarbon (PAH) precursors, which are important in the hydrocarbon-rich regions [10 and references therein]. For high temperature (highly charring), highly fire retarded and highly halogenated fuels, smoke is dominated by the non-particulates and the average value of $\xi >> 0.34$ [10 and references therein], suggesting that larger fraction of fuel carbon is converted to CO for these fuels compared to the ordinary fuels. These fuels have reduced or no hydrogen atoms in the fuel structure and it is suggested that soot is formed via the hydrogen abstraction with acetylene (i.e. carbon) addition (HACA) mechanism [10 and references therein].

Table 1. Emission rate ratios for CO to smoke for the ordinary polymers, gases and fluids and high temperature and halogenated polymers for fully ventilated combustion [6 and references therein]

Polymers/Gases/Fluids	Composition	ξ
Ordinary Polymers, Gases and Fluids		
Saturated hydrocarbons (total number 27)	C_xH_y	0.30
Unsaturated hydrocarbons (total number 21)	C_xH_y	0.36
Aromatic hydrocarbons (total number 21)	C_xH_y	0.37
Oxygenated hydrocarbons (total number 27)	$C_xH_yO_z$	0.28
Hydrocarbons with nitrogen (total number 14)	$C_xH_yN_z$	0.34
Hydrocarbons with sulfur (total number 11)	$C_xH_yS_z$	0.34
General polymers (total number 13)	$C_xH_y, C_xH_yO_z, C_xH_yN_z, C_xH_yCl$	0.36
Single automobile polymers (total number 8)	$C_xH_y, C_xH_yO_z$ and $C_xH_yN_z$	0.44
Mixed automobile polymers (total number 24)[a]	$C_xH_y, C_xH_yO_z, C_xH_yN_z, C_xH_yS_z, C_xH_yCl_z, C_xH_yF_z$	0.78
Automobile fluids (21)	$C_xH_y, C_xH_yO_z$	0.33
High Temperature Polymers		
Polyetheretherketone (PEEK)	$CH_{0.63}O_{0.16}$	1.6
Polysulfone (PSO)	$CH_{0.81}O_{0.15}S_{0.04}$	0.74
Polyethersulfone (PES)	$CH_{0.67}O_{0.21}S_{0.08}$	0.82
Polyetherimide (PEI)	$CH_{0.68}N_{0.05}O_{0.14}$	0.83
Highly Halogenated Polymers		
Chlorinated PVC	$CH_{1.3}Cl_{0.70}$	0.52
Polyvinylidenefluoride (PVDF)	CHF	0.64
Ethylenechlorotrifluoroethylene (ECTFE)	$CHF_{0.75}Cl_{0.25}$	1.1
Ethylene-tetrafluoroethylene (ETFE)	CHF	0.53
Perfluoroalkoxy (PFA)	$CF_{1.6}O_{0.01}$	13
Fluorinated ethylene-propylene (FEP)	$CF_{1.8}$	21
Tetrafluoroethylene (TFE)	$CF_{1.8}$	16

a: Some of the polymers are charring type and some are highly fire retarded. Cl: chlorinated; F: fluorinated.

In Table 1, the ξ value for the mixed automobile polymers (mixtures of ordinary, charring and halogenated polymers) is high and close to the values for the high temperature and highly halogenated polymers, suggesting that soot is probably formed by both PAH and HACA mechanisms. In a similar fashion, the ξ value of about 1.42 g/g suggested by the correlation (Fig 6 and Eq. 6) is indicative of soot formation by both PAH and HACA mechanisms for fires in general with mixed fuels. Thus, smoke emissions from fires involving mixed fuels are probably mixtures of significant amounts of soot as well as organic compounds that need to be considered for modeling and hazard assessment, rather than the common practice of considering the soot formation alone.

Smoke Composition and Color

Smoke consists of two parts, particulates and non-particulates. Soot is the dominant fraction of the particulates whereas organic compounds are the dominant fraction of the non-particulates. The following expression is derived from the mass balance for the most dominant fire products, which are CO, CO_2, particulates and non-particulates:

$$f_{CO} + f_{CO2} + f_p + f_{np} = 1 \tag{7}$$

where f_{CO}, f_{CO2}, f_p and f_{np} are the emission efficiencies of CO, CO_2, particulates and non-particulates respectively, defined as:

$$f_j = y_j /(nM_j / M_f)$$
(8)

where y_j is the yield of product j (g/g), n is the number of carbon atoms in the fuel structure, M_j is the molecular weight of product j (g/mole) and M_f is the molecular weight of the fuel monomer (g/mole). n and M_f are calculated from the elemental composition of the fuel. The particulate and non-particulate fractions in smoke, η_p and η_{np} respectively, are calculated from the following expressions:

$$\eta_p = f_p /(f_p + f_{np})$$
(9)

$$n_{np} = 1 - \eta_p$$
(10)

The values of f_p, f_{np}, η_p and η_{np} calculated from the experimental data measured in the FPA are listed in Table 2.

Table 2. Emission efficiencies and fractions of particulates and non-particulates in smoke for the fully ventilated combustion

Polymers	Composition	f_p	f_{np}	η_p	η_{np}
Ordinary Polymers					
Polystyrene	CH	0.178	0.093	0.657	0.343
Polypropylene	CH_2	0.069	0.025	0.734	0.266
Polymethylmethacrylate	$CH_{1.6}O_{0.4}$	0.037	0.020	0.649	0.351
Nylon	$CH_{1.8}O_{0.17}N_{0.17}$	0.065	0.021	0.756	0.244
Polycarbonate (PC)	$CH_{0.88}O_{0.13}$	0.149	0.277	0.350	0.650
Wood	$CH_{1.7}O_{0.74}N_{0.002}$	0.031	0.210	0.129	0.871
High Temperature Polymers					
Polyetheretherketone (PEEK)	$CH_{0.63}O_{0.16}$	0.010	0.421	0.023	0.977
Polysulfone (PSO)	$CH_{0.81}O_{0.15}S_{0.04}$	0.027	0.277	0.089	0.911
Polyethersulfone (PES)	$CH_{0.67}O_{0.21}S_{0.08}$	0.033	0.306	0.097	0.903
Polyetherimide (PEI)	$CH_{0.68}N_{0.05}O_{0.14}$	0.018	0.256	0.066	0.934
Halogenated Polymers					
Polyvinylchloride (PVC)	$CH_{1.5}Cl_{0.50}$	0.168	0.385	0.303	0.697
Chlorinated PVC	$CH_{1.3}Cl_{0.70}$	0.135	0.379	0.263	0.737
Polyvinylidenefluoride (PVDF)	CHF	0.099	0.451	0.180	0.820
Ethylenechlorotrifluoroethylene (ECTFE)	$CHF_{0.75}Cl_{0.25}$	0.114	0.426	0.211	0.789
Ethylene-tetrafluoroethylene (ETFE)	CHF	0.075	0.316	0.192	0.808
Perfluoroalkoxy (PFA)	$CF_{1.6}O_{0.01}$	0.013	0.387	0.033	0.967
Fluorinated ethylene-propylene (FEP)	$CF_{1.8}$	0.007	0.433	0.016	0.984
Tetrafluoroethylene (TFE)	$CF_{1.8}$	0.012	0.531	0.022	0.962

Measured gas concentrations and elemental compositions of the fuels were used for the calculation of f_{CO} and f_{CO2}. Measured light extinction and elemental compositions of the fuels were used for the calculation of f_p, assuming the particulates to be soot with M_j =12 g/mole in Eq. 8. f_{np} was calculated from Eq. 7. The η_p and η_{np} values were calculated from Eqs. 9 and 10 respectively.

It is well known that soot fraction in smoke depends on the hydrogen atom fraction in the fuel [2, 5, 7, 15-17]. Data used in this paper supports this as shown in Fig. 7, where the η_p values from Table 2 are plotted against the hydrogen atom mass fraction in the fuel, X_H. Data in Fig. 7 show that η_p increases with X_H and reaches a value close to unity for $X_H \geq 0.14$. For highly fluorinated polymers, there are no hydrogen atoms in the fuel structure and thus $X_H = 0$ and $\eta_p = 0$.

For the high temperature polymers with similar X_H values, η_p values are smaller than the values for the halogenated and ordinary polymers. This may due to the higher C-C atom bonds in the high temperature polymers compared to other polymers as OH concentration depends on the C/H ratio, which is a function of the number of C-C bonds. The relationship between η_p and X_H for wood in Fig. 7 is similar that for the high temperature polymers.
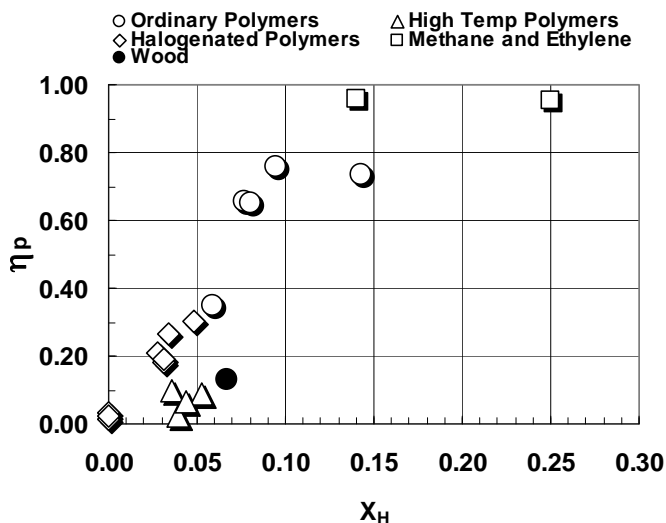

Fig 7. Particulate fraction in smoke from Table 2 versus the hydrogen atom fraction in the fuel structure. Data for methane and ethylene are from Ref. 5 and references therein.

The η_p and η_{np} values govern the color of smoke. Smoke color changes from black to white as η_p decreases and η_{np} increases. Black color of smoke is used as an indicator of smoke emission both qualitatively (visually) as well as quantitatively (optical technique), and thus polymers with higher η_p values are considered as higher smoke emitting polymers, whereas polymers with lower η_p values are considered as lower smoke emitting polymers. Figures 4 and 8 show examples of smoke emission from the combustion of a high and a low smoke-emitting polymer respectively. Figure 4 shows the combustion of high smoke emitting PVC for which $\eta_p = 0.303$ and $\eta_{np} = 0.697$ and the color of smoke is grayish black rather than completely black as 70 % smoke is soot and 30 % of smoke is a mixture of organic compounds. Figure 8 shows the combustion of low smoke emitting polyetherimide (PEI) for which $\eta_p = 0.066$ and $\eta_{np} = 0.934$ and the color of smoke is white as soot is only 7 % of smoke whereas 93 % of smoke consists of the organic compounds.

Emission Rate and Particulate and Non-Particulate Fractions in Smoke

For the development of the relationship for the average smoke emission rate given in Eq. 6, no consideration was given to the η_p and η_{np} values for the fuels. The correlation based on Eq. 6 and shown in Fig. 6, however, is for the smoke with particulates as the dominant component of smoke, as the light extinction data were used, which provide data mainly for the particulates. Data for the polymers for which non-particulates were the dominant components of smoke, were not used in Fig. 6, as they showed deviations from the correlation. These included data for single fuels with little or no hydrogen atoms in the structure, such as fluorinated ethylene-propylene, FEP, and high temperature polymers and data for $\Phi >$ 0.70. The smoke compositions for these types of fuels for the fully ventilated combustion are listed in Table 2.
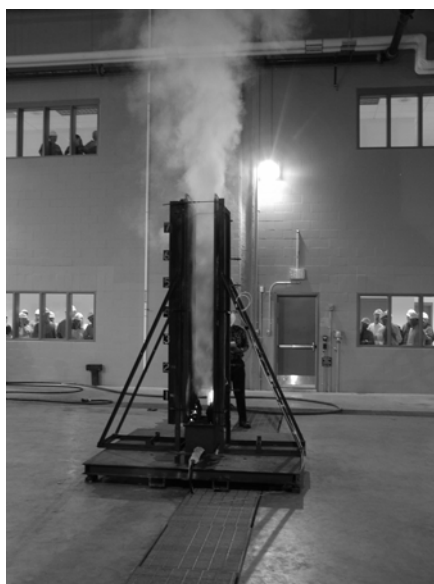
Fig 8. Combustion of low smoke emitting 2.4-m high and
0.60-m wide polyetherimide panels under the 5 MW FPC.

Ventilation also affects the η_p and η_{np} values. The high η_p values for the ordinary polymers for fully ventilated combustion decrease as conditions change to under-ventilated or fuel-rich (increase in the Φ value) and become comparable to the values for the high temperature and highly halogenated polymers (Table 2). For example, for methane and ethylene, the high η_p values for the fully ventilated combustion decrease significantly and η_{np} values become high for the under-ventilated combustion, as shown by the data listed in Table 3 that are taken from Ref. 5 and references therein.

Table 3. Mass concentration and emission efficiencies of particulates and non-particulates in non-premixed flames of methane and ethylene (data are taken from Ref. 5 and references therein)

Φ	$m_p(\mu g/cm^2)$	$m_{np}(\mu g/cm^2)$	η_p	η_{np}
Methane				
1.0	21	1.0	0.94	0.06
2.0	4.9	8.4	0.30	0.70
4.0	0.4	3.4	0.08	0.92
4.0	1.0	5.2	0.13	0.87
Ethylene				
0.5	19	0.7	0.96	0.04
1.0	27	1.3	0.95	0.05
2.0	15	7.2	0.64	0.36
4.0	6.2	7.0	0.43	0.57

For methane for $\Phi = 4$, smoke emission is lighter in color (yellowish appearance) than the smoke emission at $\Phi = 1$ [5 and references therein]. This confirms the higher η_{np} value at $\Phi = 4$, listed in Table 3. For ethylene at $\Phi = 4$, soot particles agglutinates indicating presence of liquid-like component which is not present at $\Phi = 1$ [5 and references therein]. This also confirms the higher η_{np} value at $\Phi = 4$, listed in Table 3.

SUMMARY

1. Smoke emission rate, $\dot{G}_S$, depends on the fire size that can be represented by the chemical heat release rate, $\dot{Q}_{ch}$, and the combustion chemistry governed by the generic nature of the fuel that can be represented by the emission rate ratio of CO to CO_2 (or the ratio of their yields) $(\dot{G}_{CO}/\dot{G}_{CO2})$;

2. The experimental data supports this dependency as a good correlation is found between the average values of $\dot{G}_S$ for particulate dominated smoke and $\dot{Q}_{ch}(\dot{G}_{CO}/\dot{G}_{CO2})$ with $\dot{Q}_{ch}$ in the kW to MW range and an order of magnitude variation in the $\dot{G}_{CO}/\dot{G}_{CO2}$ values for the fully ventilated, normal air combustion of fuels in smaller- to larger-scale pools and parallel panels;

3. Deviations are found in the correlation for single fuels with reduced or no hydrogen atoms in the structure, such as the high temperature and highly halogenated polymers and for the under-ventilated combustion conditions, where smoke is dominated by the mixture of non-particulates. The reason for this deviation appears to be due to the unaccountability of the non-particulates in the measurements for smoke using the optical technique (developed mainly for the particulates or condensed non-particulates);

4. The correlation holds for the combustion of single fuels, with reduced or no hydrogen atoms in the structure, in the presence of fuels that supply H and OH atoms such as by the propane gas burner in the parallel panel;

5. The correlation is expected to hold for all types of fuels and conditions if an experimental technique can be used that would account for both particulates and non-particulate components of smoke. This generalized correlation would be useful for fire modeling and for the smoke hazard assessment.

REFERENCES

[1] Manahan, S.E., *Environmental Chemistry*, 6th edition, Lewis Publishers, 1994;

[2] Glassman, I., "Soot Formation in Combustion Processes", *22nd Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1988, pp. 295-311.

[3] Hamins, A., "Soot", Chapter 3 in *Environmental Implications of Combustion Processes*, Puri, I.K. (editor), CRC Press, Boca Raton, Florida, 1993, pp. 71-95.

[4] Pitts, W.M., (1995) The Global Equivalence Ratio Concept and the Formation Mechanisms of Carbon Monoxide in Enclosure Fires, *Prog. Energy Combust. Sci*, **21**, 197-237, doi:10.1016/0360-1285(95)00004-2.

[5] Santoro, R.J., "Fundamental Mechanisms for CO and Soot Formation", Technical Report NIST-GCR-94-661, National Institute of Standards and Technology, Gaithersburg, MD, November 1994.

[6] Tewarson, A., "Generation of Heat and Chemical Compounds in Fires", *The SFPE Handbook of Fire Protection Engineering,* Third Edition, Chapter 4, NFPA, Quincy, MA 2002, pp. 3-82 to 3-161.

[7] Puri, R., and Santoro, R.J., "The Role of Soot Particle Formation on the Production of Carbon Monoxide in Fires", Fire Safety Science, *Proceedings of the Third International Symposium*, Elsevier Applied Science, London, 1991, pp.595-604.

[8] Koylu, U.O., Sivathanu, Y.R., and Faeth, G.M., "Carbon Monoxide and Soot Emission from Buoyant Turbulent Diffusion Flames", Fire Safety Science, *Proceedings of the Third International Symposium*, Elsevier Applied Science, London, 1991, pp. 625-634.

[9] Mulholland, G., Yusa, S., Janssens, M., Twilley, W., and Babrauskas, V., "The Effect of Oxygen Concentration on CO and Smoke Produced by Flames", Fire Safety Science, *Proceedings of the Third International Symposium*, Elsevier Applied Science, London, 1 1991, pp. 585-594.

[10]   Tewarson, A., and Khan, M.M., "Carbon Monoxide and Smoke Emissions in Fires", *Interflam 2007*, Interscience Communications, London, 2007, pp. 1059-1070.

[11]   Khan, M.M., Bill, R.G., and Alpert, R.L., 2006, Screening of Plenum Cables Using a Small-Scale Fire Test Protocol, Fire and Materials, 30, pp. 65-76, doi:10.1002/fam.899.

[12]   Nam, S., De Ris, J., Wu, P., and Bill, R., "From Bench-Scale Test Data to Predictors of Full-Scale Fire Test Results", *Proceedings of the Eighth International Symposium*, The International Association of the Fire Safety Science, London, 2005, pp.469-480.

[13]   Nam, S., "Intermediate-Scale Fire Test---Stepping Stone for Prediction of Material Flammability in Real-Scale Fire Through Bench-Scale Fire Test Data", *7th Asia-Oceania Symposium on Fire Science & Technology,* Hong Kong International Trade & Exhibition Center, 2007, September 20-22,

[14]   Tewarson, A., "Thermophysical and Fire Properties of Automobile Plastic Parts and Engine Compartment Fluids", Technical Report #0003018009, Volume III, Motor Vehicle Fire Research Institute, Charlottesville, VA 2005 (www.mvfri.org).

[15]   Brezinsky, K., Hura, H.S., and Glassman, I, 1988 Oxidation/Pyrolysis Chemistry as Related to the Fuel Sooting Tendencies, *Energy and Fuels*, 2, 487-493, doi:10.1021/ef00010a015.

[16]   Gomez, A, Sidebotham, G., and Glassman, I, 1984 Sooting Behavior in Temperature-Conrolled Laminar Diffusion Flames, *Combustion and Flame*, **58**, 45-57, doi:10.1016/0010-2180(84)90077-4.

[17]   Wagner, H.Gg., "Soot Formation-An Overview", in *Particulate Carbon, Formation During Combustion,* S.C.Siegla and G.W. Smith (Editors), 1981, Plenum Press, New York, NY, pp 1-29.