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PVC Sheathed Electrical Cable Fire Smoke Toxicity

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ABSTRACT

The cone calorimeter, under free and restricted ventilation conditions, was used to investigate the toxic emissions from PVC cable fires. Toxic gases were measured using direct high temperature gas sampling from the exit of the cone calorimeter with a short chimney attached to the exit from the electrical cone. Toxic species CO and HCl were identified as a function of time using a heated Gasmet FTIR. The particle number was determined using the Cambustion DMS500 fast response particle sizer with a diluted sample taken from the diluted cone calorimeter exhaust flow at the same location as the optical obscuration smoke meter. The HCl concentrations from the Chlorine in the PVC sheath demonstrated HCl levels well above the LC_{50} concentration for HCl. The restricted ventilation reduced the peak fire heat release rate and the peak toxicity and HCl occurred later than for free ventilation. The equivalence ratio in the gases from the combustion zone, were both rich at 1.5 for free ventilation and 1.3-1.4 for restricted ventilation. The toxicity results showed the classic phases of compartment fires: growth, steady state burning and then fire decay. After flaming combustion was extinguished, slow char combustion continued with high CO emissions. The particle size distribution showed peak particle number, PN, nuclei mode particles at 10 nm and an accumulation mode at 100 nm. The number of particles at 10 nm for free and restricted ventilation were extremely high and showed that the freely ventilated fires had the highest PN, but later in the fire the restricted ventilation PN were higher. Nano-particle emissions < 50 nm from PVC fires are a health hazard that is currently unrecognized and unregulated.

KEYWORDS: Fire toxicity, compartment fires, electrical cable fires, PVC, particle.

INTRODUCTION

Deaths in fires are mainly due to toxic gases breathed in during exposure to fire smoke [1], yet there is no requirement to measure the toxic gases (other than smoke obscuration) from materials as part of their approval for use in buildings [2]. The Grenfell Tower fire in London in 2017 had toxic smoke emissions as a major cause of death and many survivors had to have their lungs flushed out to remove black carbon deposits [3]. To reach the lungs particles have to be < 100 nm diameter and yet there is hardly any information on the particle size distribution of particulate material generated in fires. The medical effects of ultra-fine particles that cause lung and heart related problems within days of exposure [4-8] are well known in atmospheric pollution, but the exposure to very high levels of fine particles in fires can be much greater in a short time than exposure to fine particles in the a poor quality atmospheric exposure in roadside air pollution, where concentrations are around $50\mu g/m^3$ compared with over 2000 times this concentration in fires [9]. This means that a one minute exposure to fire particulates during escape is equivalent to a full day exposure to roadside air pollution, with most fires giving a higher exposure than this. Escape times are at least 10 minutes, often walking through significant smoke concentrations. This work presents data on particle number

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in PVC cable fires as well as toxic gas emissions. Fine particulates are shown to be a significant contribution to smoke in building fires and could be formed as HCl droplets.

Polyvinyl Chloride (PVC) is the second most important fire load after wood [10] and PVC sheathed electrical cables are the most common source of PVC in fires. It has been estimated that there are 250m of electrical cable per house (50m per room) and 140 fires/million km cable/year [10]. Electrical cable fires may occur as part of a fire load for a fire that has started elsewhere and spread to ignite the cables externally. This is simulated in the present work using the cone calorimeter to represent radiant heating from a fire that engulfs the cables. There is no requirement in material approval tests for electrical cables to have any toxicity measurements, other than the visible obscuration that smoke generates [2].

One of major applications of PVC in buildings is in electrical cables, as the electrical insulation sheath. However, in building products PVC is widely used, for example clear sheets, skirting boards and roofs. PVC is also used in other electrical components such as computers, electrical cords or cables, component housing and phone system [11]. About 8% PVC, about 40 million tons of worldwide production capacities each year was used for cable production between 2006 and 2017 [12, 13]. Chlorine based material with a high chlorine content (>56%) are classified as fire retardant and widely used in many applications because it can prevent or slow down the burning process [14]. However, it can produce toxic gases, mainly hydrogen chloride (HCl), when burnt, which is an irritant depending to the concentration level. Irritancy effects due to exposure to HCl can impair or reduce the escape ability of occupants during the fire. Fire-retarded substances can increase smoke toxicity more than they reduce fire growth rate [15].

Sundstrom [2] has reviewed methods of testing of cables for their fire resistance and concluded that current tests concentrate on fire propagation rates and not on toxicity. However, he concludes that the future must address the toxicity issue and the measurement requirements, as reliable test methods are lacking. Hirschler [16, 17] has compared the large scale cable tray fire tests of ASTM D921 and IEC 332-3 with the cone calorimeter [18] and concluded that the heat release rate, HRR and smoke production measured in the cone calorimeter can be used to predict the results of the larger scale tests. This was the reason for the use of the cone calorimeter in the present work. A very small number of studies of toxic gases and particulate emissions in fires have involved electrical cables and polymer fires and particle size measurement [19-22].

Al-Sayegh et al. [21] have used the cone calorimeter with PVC cables with free ventilation, with heated gas sampling and analysis, using the Gasmet FTIR, of the toxic gases from the diluted products of the fire at the same location as the smoke meter. Their work showed that at 40 kW/m^2 radiant heat the toxic yields peaked at the time of peak HRR and were 0.18 for CO, 0.4 – 0.5 for HCl, 0.04 – 0.05 for Acrolein and 0.02 – 0.03 for Formaldehyde. The relative toxicity on an LC_{50} basis showed that of the total toxicity 20% was from HCl, 41% from Acrolein and 33% from Formaldehyde. On a $COSHH_{15min}$ basis, which is important for no impairment of escape, HCl was 33% of the total toxicity, Acrolein was 53% and Formaldehyde was 12%. In both cases the contribution of CO to the toxicity was small, but this could be due to the diluted combustion and post flame oxidation. The present work sampled directly from the hot gases at the exit from the cone calorimeter and so post flame oxidation of toxic gases was avoided. However, the conclusion from the work of Al-Sayegh et al. [21] was that the main toxic gases on an LC_{50} or $COSHH_{15min}$ basis were Aldehydes and that the toxicity of HCl was only 20% (LC_{50}) or 33% ($COSHH_{15min}$) of the toxic gas problem. The HCl yields were shown by Al-Sayegh et al. [21] to be higher than most previous work, especially in small scale tests such as the Purser furnace test [23, 24]. However, the agreement was very good with the previous cone calorimeter work of Babrauskas et al. [25] for PVC sheet samples. However, the HCl yields were significantly lower than the 100% conversion of Chlorine to HCl, which gives a yield of 0.58. The reason for this was shown by Al-Sayegh et al.

[21] to be due to Chlorine remaining in the char at the end of flaming combustion. Al-Sayegh et al. [22] have also burnt PVC cables with a pine wood crib fire in a 1.6m^3 compartment fire. They showed that the yield of HCl was 0.3 – 0.35 which is a little lower than the 0.4 – 0.5 yield for the cone calorimeter [15], but still higher than most values for HCl yield in the literature [21].

EXPERIMENTAL EQUIPMENT

The cone calorimeter (ISO 5660) [18] is a standard bench scale piece of equipment designed to measure the heat release rate and flammability properties of materials. The authors have adapted the standard cone calorimeter [18] for raw gas toxicity and particle size measurements from the cone heater outlet, for both the free and restricted ventilation. The modified calorimeter and associated instrumentation is shown in Fig. 1. The restricted ventilation version of the cone calorimeter uses an airtight stainless-steel box set up to create restricted ventilation combustion conditions. It was operated with a controlled air supply design to create rich combustion conditions that occur in air starved compartment fires. The load cell, sample holder and cone heater were enclosed in the steel box, which had a metered air supply through the bottom of the air tight box. The airtight box was 38 cm long, 30 cm wide and 33 cm high, with a volume of 0.0376 m^3. In the process of developing this experimental method it was observed that there was excessive heat loss from the metal box, which influenced the temperature of the test specimen and hence influenced the HRR. The airtight box design was improved by insulating the inside walls and the door was insulated from the outside. An insulation board 25mm thick was used to avoid heat loss. The combustion process was observed through a glass window on the cone calorimeter enclosure which was also insulated, when not being used for viewing the flame. An insulation board was also placed in the sample holder underneath the test specimen to prevent heat losses to the supporting metal cylinder leading to the load cell heating.

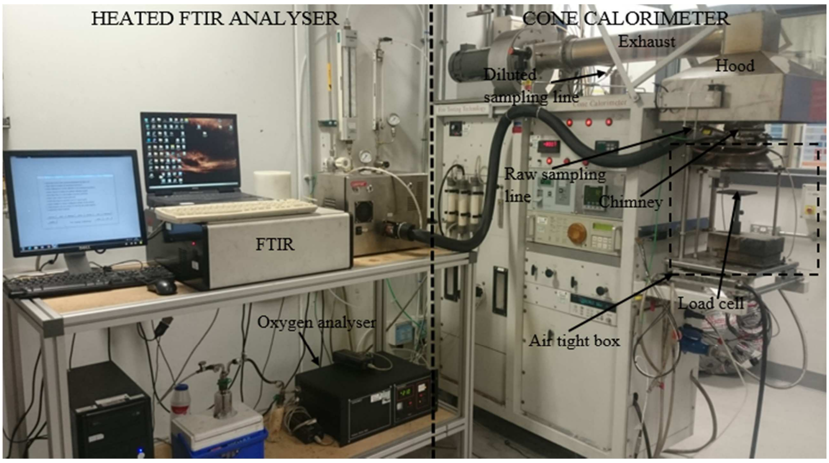

Fig. 1. Configuration of the cone calorimeter and FTIR analyser.

The airflow introduced to the combustion chamber was from a compressed air supply and was measured using a variable air flow meter with the air flow varying from 6 – 28 L/min. This variable airflow translates to 0.12 – 0.56 g/s air mass flow. A more general parameter is considered to be the air mass flow per exposed surface area of the test specimen (0.01m^2) and this converts to 12 – 56 g/sm^2 in these terms. The simple assumption that for all fuels there are 3.05 MJ of heat release per kg of air is another way of representing the ventilation conditions. This translates the air mass flow range into fire HRR in kW as 0.37 – 1.71 kW fires and in terms of the exposed surface area of the wood is 37 – 171 kW/m^2. In the present work a single air flow was used of 19.2 g/sm^2 or 59 kW/m^2

for the restricted ventilation condition. This is the maximum possible heat release rate (HRR) in the primary fire in the enclosed compartment.

A radiant heat level of 35 kW/m^2 was used for both the free and restricted ventilation tests. This is the recommended standard heat flux by British Standards [18] for use in material evaluation for performance in fires using the standard cone calorimeter [18]. Also, 35 kW/m^2 was recommended by Flecknoe-Brown et al. [26]. Herzberg and Blomqvist, [19] noted that 35 kW/m^2 was a "trade-off between a lower value, which possibly would have caused material pyrolysis only, and a higher value which might have provoked an unrealistically clean burning behaviour". This radiant flux was a little lower than the 40 kW/m^2 used in the work of Al-Sayegh et al. [21] where 40 kW/m^2 was used. However, they investigated 20, 30 and 40 kW/m^2 and 20 and 30 were too low to lead to ignition of the PVC, but the 35 kW/m^2 was not tested and this did give ignition of PVC in the present work. The temperature of the cone was about 700^{o}C for the 35 kW/m^2 irradiation level.

Test sample preparation

BS 6004 6242Y Prysmian A electrical cable with PVC insulation and sheath [27] were cut into 100mm strips and a single layer of 7 pieces filled the 100mm square test section of the cone calorimeter, as shown in Fig. 2. Only one side of the cable was exposed to the cone heater during the burning test. The initial mass of cables were weighed, as a check on the value measured by the cone calorimeter load cell.

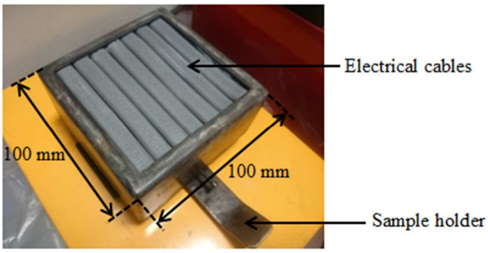

Fig. 2. PVC electrical cables in sample holder.

Heated Fourier-Transform Infrared Spectroscopy

The heated Gasmet FTIR analyser was calibrated by the manufacturer for 60 species, including all major toxic species in fires. Also a diluted gas sample was sent from the cone calorimeter collection duct for particle size analysis using the Cambustion DMS500 [28]. The overall experimental rig of the cone calorimeter and portable analysers used is shown in Fig. 1.

Cambustion DMS500 particle size analyser

For particle size analysis a diluted sample is required for two reasons. Firstly, the dilution lowers the dew point by cooling and reducing the concentration and this prevents water vapour from the combustion products appearing as droplets and being counted as particles. However, higher molecular weight unburned hydrocarbons from the fire can form liquid aerosols in the dilution process and these are part of the particles that may be a health hazard. If the fire forms acidic gases then with the water vapour present acid droplets can form, for example Hydrocholric acid droplets will form in the present work. For total particle size analysis it is not known whether particles in any size range are liquid or solid or a mixture of both. The second reason for particle number size distribution needing to be measured in a diluted sample is that for low dilution particles agglomerate in the sampling system and the size distribution changes and the number of particles is reduced. Usually a dilution ratio of around 100/1 or more is advocated [29, 30]. The cone calorimeter dilutes the products of combustion from the cone heater outlet (chimney outlet in the present case) with ambient air. Thus a diluted gas sample for particle size analysis taken from the cone calorimeter dilution tunnel is the obvious choice of gas sample location. The sample point was close to where the smoke production was measured in the cone calorimeter using the standard obscuration meter, so that particle number and smoke obscuration can be directly compared. It was shown above that at the present test conditions the dilution ratio was 112/1 and hence meets Kittleson's [29, 30] recommended dilution ratio of >100/1.

The Cambustion DMS500 (Differential Mobility Spectrometer) [28] particle size measurement equipment was used to measure real time particle sizes in the size range 5 – 1000 nm. The DMS500 size separates particles on the basis of their electrical mobility and the size may be different from an aerodynamic mobility analyser. Electrical mobility is the dominant mode of particle size measurement for nano-particles. It is a transient instrument and can take several size distributions per second. In the present work the size distribution as a function of the fire time duration was measured.

Initial analysis of PVC Prysmian A electrical cable

Shimadzu TGA-50, CHNS Thermo AE2000 and PARR 6200 Bomb Calorimeter were used to determine its chemical composition, energy content, volatiles, moisture, fixed Carbon and ash contents. Table 1 shows the results for the PVC cable composition. The stoichiometric A/F was computed by carbon balance from the elemental composition. Chlorine was not determined, but was assumed to be the missing mass from the elemental analysis. The chemical formula in Table 1 was close to that of PVC but the Hydrogen was significantly lower, indicating that this was not a pure PVC cable sheath but had some other hydrocarbons mixed in. As the CH_y had y too low, this indicates the use of low H/C ratio polymers in the electrical sheath material.

Table 1. Pre-analysis results for PVC Prysmian A electrical cable (BS6004)

Analyser	Parameter	Data/Value
Thermogravimetric analyser	Proximate analysis (wt.%)(daf)	
	Volatile matter	96.36
	Fixed Carbon	3.64
	Moisture (as received)	0.40
	Ash (as received)	28.91
CHNS analyser	Ultimate analysis (wt.%)(daf)	
	Carbon	35.63
	Hydrogen	3.84
	Chlorine	60.53
Bomb calorimeter	GCV (MJ/kg)	17.95
Other information		
	Stoichiometric A/F	4.85
	Chemical formula (daf)	$CH_{1.29}Cl_{0.57}$
	Pure PVC	$CH_{1.5}Cl_{0.5}$

For TGA analysis, the test sample was heated to 920°C in Nitrogen. The process removes fixed Carbon. At 920°C Nitrogen was change to air to burn the fixed Carbon. The balance from the total of 100% mass after deduction of moisture, volatiles and fixed Carbon was ash. The TGA mass loss in Nitrogen is shown as a function of temperature in Fig. 3 and compared with that of Al-Sayegh et al. [21], where there is good agreement. The release of HCl occurs between 250 and 300°C.

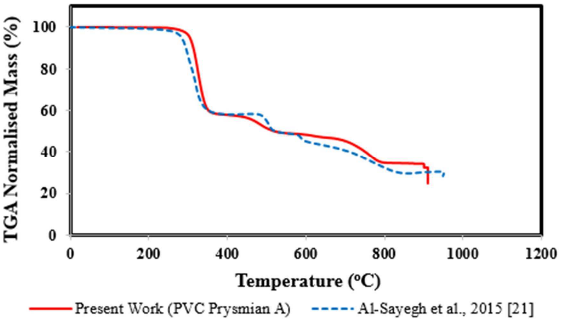

Fig. 3. Normalised mass loss as a function of temperature from TGA analysis.

The elemental analysis gave 60% of the PVC mass as Chlorine; this would produce a yield of HCl of 62%. Fig. 3 shows there was a 42% weight loss due to HCl loss in the temperature range 250 – 300°C. However, there is evidence of another volatile loss at 400-500°C and assuming that this is also HCl. The total weight loss due to release of HCl is 52% close to the expected total yield of HCl. Bowes [31] commented that 70% of the expected HCl yield (41%) occurs rapidly at 272°C and this was also found in Fig. 3.

An SEM model of Carl Zeiss EVO MA15 was used to perform a full elemental analysis. The SEM analysis showed that other than Chlorine there were the flame retardant minerals Aluminum and Calcium. Mineral type flame retardants are added to polymers, including the modern cables, to inhibit combustion and smoke production [32]. It is likely in this case that Calcium carbonate was added as a thermal inert that would decompose to release CO_2 in a fire. This was the cause of the long ignition delay in the tests.

RESULTS

Heat release rate, fire equivalence ratio and combustion efficiency

The heat release rate by oxygen consumption and the fire equivalence ratio from carbon balance are shown in Fig. 4 and Fig. 5 respectively. These show that the ignition delay at 35 kw/m^2 radiant heat was about the same for free and restricted air ventilation at 22s.This compares with about 50s in the work of Al-Sayegh et al. [21]. These relatively short ignition delay indicate little effect of any fire retardant for the PVC cables.

Fig. 4 shows the primary heat release by Oxygen consumption for the cone calorimeter chimney gas sample. The primary HRR with restricted ventilation was higher than that for free ventilation and at its peak was close to that for the theoretical HRR if all the Oxygen in the air was consumed, 59 kW/m^2. The reason for the higher primary HRR was the higher temperature of the confined restricted ventilation fire which gives higher combustion efficiency. The total primary and secondary combustion HRR is also shown in Fig. 4, based on the standard cone calorimeter Oxygen consumption method. The difference from the primary HRR is the secondary combustion HRR, which occurs as the gases from the chimney on top of the cone heater are discharged and entrain air when secondary combustion can occur. The secondary HRR is small but significant and equal for free and restricted ventilation. This is the main reason that the cone calorimeter with toxic gases measured at the same location as the smoke meter is not deemed [33] to be a good experimental device for toxic gas emissions, as the secondary oxidation may reduce the toxic emissions or generate other emissions such as the partial oxidation Aldehyde gases. The free ventilation total

HRR is still lower than that for restricted ventilation, although at the highest HRR there was very little difference. These Oxygen based overall HRRs are shown in Fig. 4 to be substantially lower than the HRR based on the PVC cable mass loss, particularly at the start of combustion. The reason is that HCl mass loss has no heat release and the poor efficiency of secondary combustion.

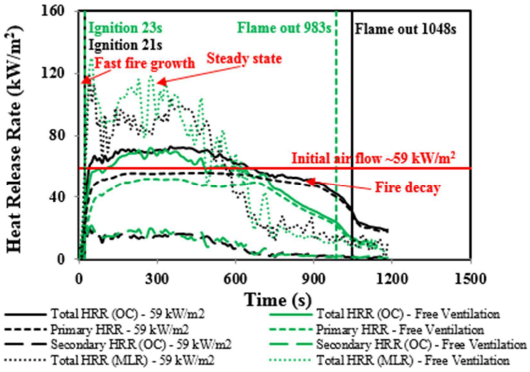

Fig. 4. Heat release rate against time.

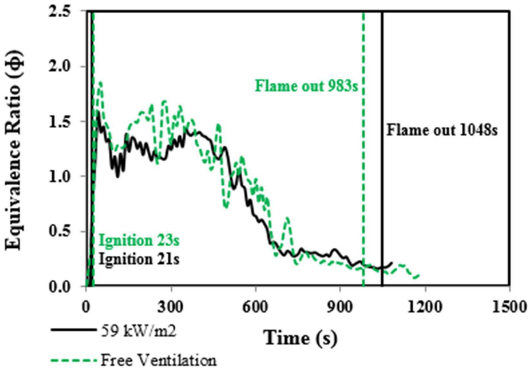

Fig. 5. Equivalence ratio against time.

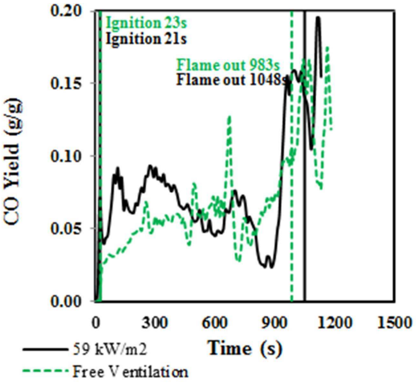

Fig. 6. CO yield as a function of time.

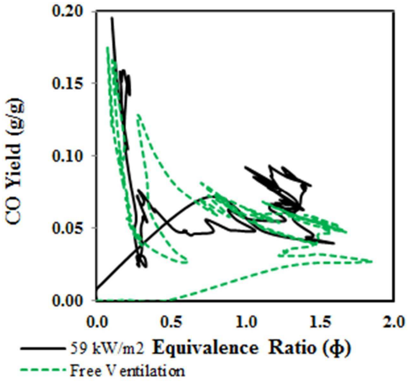

Fig. 7. CO yield as a function of ϕ.

Figure 5 shows that in the region of the highest HRR in Fig. 4, the primary equivalence ratio, ϕ, was rich for both free and restricted ventilation. Surprisingly ϕ was richer for the free ventilation case due to the higher oxygen availability which enabled more fuel to burn which created richer mixtures. However, the lower HRR was due to the richer mixture and the associated lower temperatures. For both free and restricted ventilation the HRR reduced after 450s and the equivalence ratio became lean after 550s. The high HRR up to 450s is associated with the rapid release of flammable volatiles from the PVC cables and the slower later HRR is char combustion of the residual material. This later burning lean phase was the source of the highest yields of CO and THC, as shown in Figs. 6 and 8, which gave a poor combustion efficiency as shown in Fig. 9. The CO yield as a function of ϕ in Fig. 7 shows that the lean mixtures were the greatest region of high CO yield. This was not expected as rich mixtures normally have high CO due to equilibrium chemistry. However, in this case the poor combustion efficiency dominated the production of CO. Aljumaiah et al. [34] have shown for pool fires that CO yields were high for lean low temperature pool fires in restricted ventilation enclosures, due to poor combustion efficiency.

Figure 10 shows the HCl yield as a function of time for free and restricted ventilation fires. Fig. 11 shows the HCl yield as a function of ϕ and there was no correlation for both ventilations. The yield peaked for both ventilations at 0.1, which is well below the theoretical yield of 0.58 and lower than the 0.2 – 0.3 peak yield found by Al-Sayegh et al. [21] for a different PVC cable. Their work sampled the toxic gases after dilution for free ventilation fires. Fig. 10 shows that the peak HCl yield occurred at different times for the two ventilations. It peaked at 300s for the restricted ventilation case and at 700s for the free ventilation case. Other toxic gases also had the same features of later generation with free ventilation. The reason for this difference is not known as there was no significant difference in the HRR or the equivalence ratio at these times. Al-Sayegh et al. [21] had the peak HCl yield 100-200s after ignition, which was much sooner than that in Fig. 10 for both ventilations. It is possible that the fire retardant in the cables delayed the release of HCl, but this would not explain the different times for the release of HCl for the two ventilations.

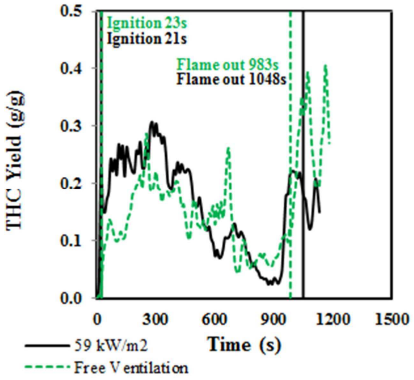

Fig. 8. THC as a function of time.

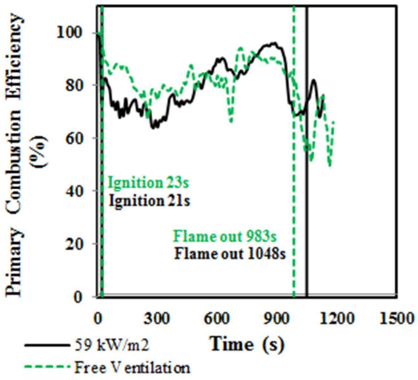

Fig. 9. Primary Combustion Efficiency against time.

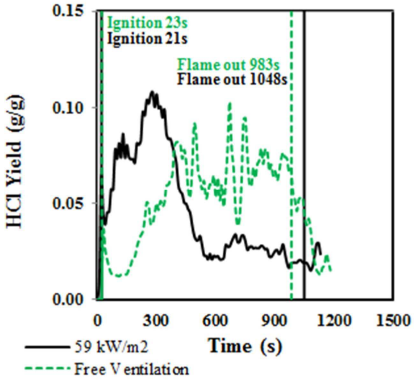

Fig. 10. HCl yield for free and restricted ventilation.

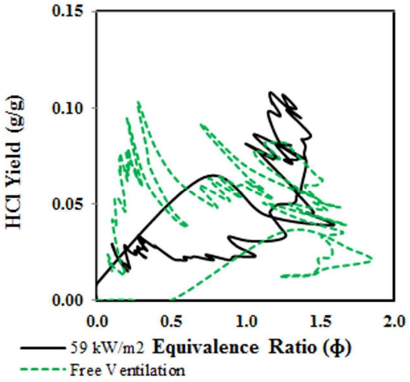

Fig. 11. HCl yield as a function of ϕ.

Al-Sayegh et al. [21] reviewed the published yields for CO and HCl in the literature for PVC fires, most of which were not PVC cable fires. Babrauskas et al. [25] for the standard cone calorimeter found the HCl yield to be 0.3 with the CO yield at 0.07 which is three times the HCl yield in the present work. However, the present yields for CO and HCl were similar to some in the literature such as the 0.09 HCl yield of Bowes [31] and the 0.045 – 0.13 yield for HCl of Blomqvist et al. [35], who also had a CO yield of 0.04 –0.13 which is similar to the present range in Fig. 6. Hull et al. [24] used the Purser furnace with HCl yields of 0.11-0.15 and CO yields of 0.025 – 0.12, both of which are similar to the present results.

Particle size distributions

Figure 12 shows the particle size distribution as a function of time for the free and restricted ventilation PVC cable fires. For free ventilation there was a nuclei mode peak number at 20 nm and an accumulation mode peak number at 500 nm. The size distribution was more varied for restricted ventilation and there were three size peaks at 20, 200 and 500 nm. After the flame went out the 500 nm peak did not occur but the 20nm nuclei mode was still present at the highest values. For restricted ventilation there was a large variation in the 20 nm nuclei peak particle number, whereas for free ventilation the 20 nm number had a much smaller variation. The 20nm size range is that with the worst health effects [4-8], but all the particles below 50 nm have a health effect [4-8]. It is likely that the 20 nm particle size was contributed to by HCl aerosols from the large concentration of HCl. Fig. 10 shows that HCl peaks later in the fire for free ventilation and this is where the peak accumulation mode particle number occurred. HCl peaked early with restricted ventilation and the 20 nm particles occurred earlier.

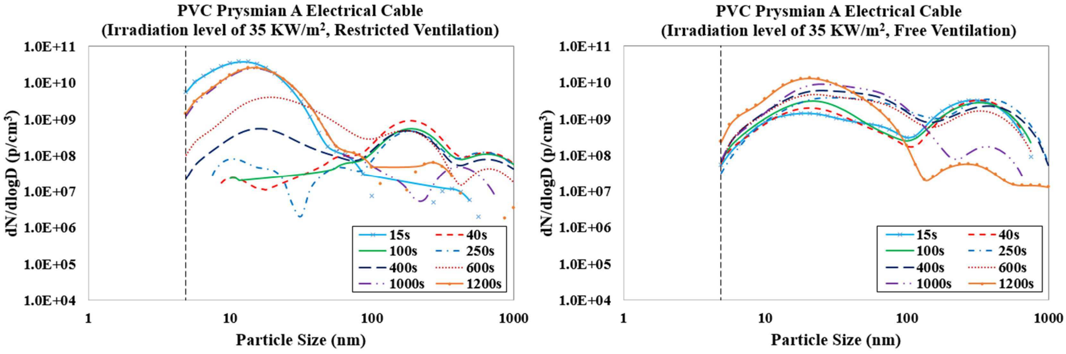

Fig. 12. Particle number distributions for free and restricted ventilation for various times.

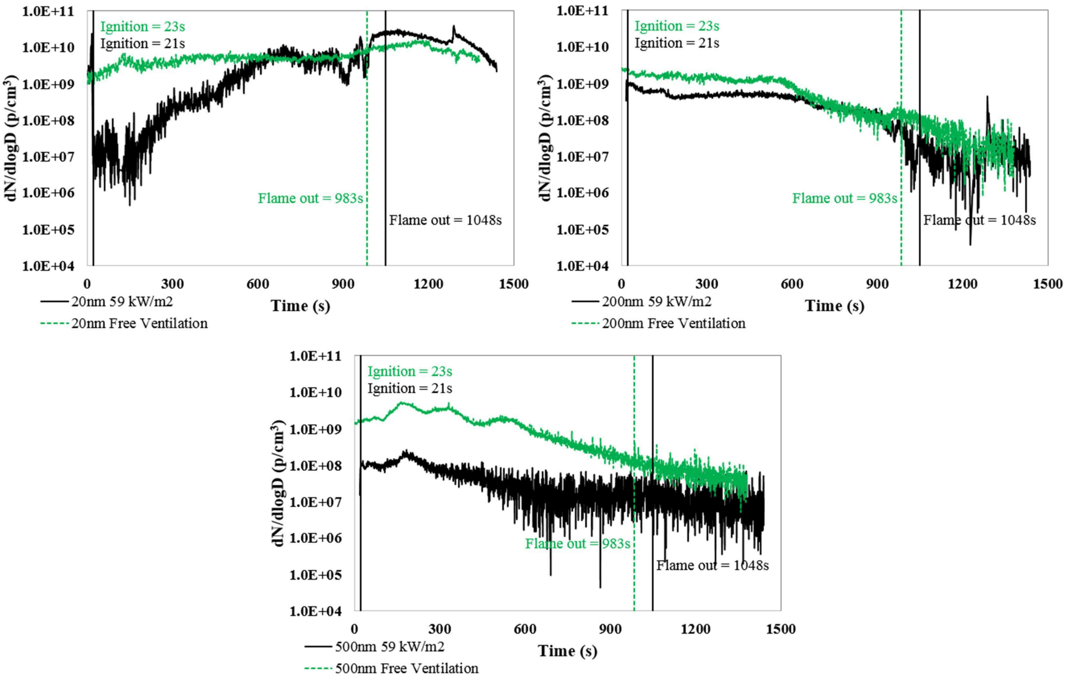

Fig. 13. 20, 200, and 500 nm particle numbers against time for free and restricted ventilation.

Figure 5 shows that up to 500 s the fire was rich for both ventilations and this would lead to high soot formation, so that the 20 nm particles could be Carbon from rich combustion. The free ventilation results in Fig. 5 were richer for the first 400 s and this would produce higher Carbon nuclei particles. In the same period the primary HRR was lower for the free ventilation case and this would produce lower temperatures and lower soot oxidation rates. A feature of the free ventilation results in Fig. 12, which is unusual in combustion size distributions, was the very high number of coarse particles with a peak at 500 nm. This indicates high mass emissions would occur. However, it is the high number of 20 nm particles that would cause the most harm to those exposed to this smoke.

The number of particles at the three size peaks in Fig. 12, 20, 200 and 500 nm, are shown as a function of time in Fig. 13 for free and restricted ventilation. This shows that for all size ranges the free ventilation fire was much higher in particle number for the first 600 s of the fire, where the HRR was highest and the combustion was rich. The 500 nm number was much higher for free ventilation and this may have been due to the late generation of HCl, shown in Fig. 10. Coagulation may have been faster in the absence of HCl vapour condensation, which would occur earlier in the restricted ventilation fire.

CONCLUSIONS

The cone calorimeter, with restricted ventilation and raw gas cone exit toxic gas measurements, is a good test method to access fire materials for gaseous toxicity and particulate emissions. For gaseous species, primary heat release rate and equivalence ratio the difference between free and restricted ventilation was small. However, the release of HCl was quite different with this occurring later after the main HRR period for free ventilation. There were major differences in the particle size distribution and the peak numbers. The free ventilation fire had much high coagulation particle number as well as high 20 nm particle number. The high number of coagulation particles may have been due to the low HCl in the high HRR period of the fire.

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