

# HCN Yields and Fate of Fuel Nitrogen for Materials under Different Combustion Conditions in the ISO 19700 Tube Furnace and Large-scale Fires

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## ABSTRACT

For calculations of time-concentration curves for toxic products in full-scale fires it is necessary to know how the yields of key toxic species vary with combustion conditions and fuel composition. In this paper, the relationships between equivalence ratio ( $\phi$ ) and HCN yields and conversion efficiencies (mass fraction of fuel nitrogen released as HCN) are presented for ten common nitrogen-containing materials and products combusted in the ISO19700 tube furnace under steady flaming conditions at a furnace temperature of 650-700°C in air. Additional experiments were carried out at 850°C and also in 10% and 12% oxygen. Large-scale fire tests were carried out under well-ventilated and vitiated combustion conditions on three materials for comparison. For non-FR materials sigmoid relationships between  $\phi$  and HCN yields were found with very low yields (0.00003-0.002 g/g) at  $\phi$  0.5 increasing to a wide range (0.0036 g/g to 0.11 g/g) at  $\phi$  2 depending upon the material. Yields from some materials were also found to be sensitive to furnace temperature and oxygen concentration. When normalised for nitrogen content, the relationships between  $\phi$  and HCN recovery were more similar, falling into high (maximum HCN recovery fraction ~ 0.16) and low groups (maximum 0.085). Although the large-scale test data were more variable, a good agreement was found with the tube-furnace results.

**KEYWORDS:** fire chemistry, hydrogen cyanide, yields, modeling, performance-based design, compartment fires, toxicity, hazard evaluation

## INTRODUCTION

In full-scale fires, occupant tenability depends upon the time-concentration curves for the main toxic fire effluents. For engineering ASET (Available Safe Escape Time) calculations, inputs are necessary both for fire growth rates and for smoke and toxic product yields under different fire conditions [1,2]. Existing methods often consider only smoke density and/or carbon monoxide, with yields often treated as constants, usually for the well-ventilated fire case [1,3]. However, the yields of some key toxic products, particularly carbon monoxide, hydrogen cyanide and organic irritants (such as acrolein, formaldehyde and related compounds), have been shown to be highly dependent upon combustion conditions, while others, particularly acid gases and to some extent smoke particulates, are less so [1,4]. For flaming fires, an important yield determinant is the fuel/air ratio, represented by the equivalence ratio ( $\phi$  [ $\phi$ ]), expressed in terms of the actual fuel/air ratio divided by the stoichiometric fuel/air ratio [4-6]. For example, the yield of carbon monoxide can increase by up to a factor of approximately 50 between well-ventilated flaming conditions ( $\phi < 1$ ), and fuel rich conditions ( $\phi > 1$ ) [2,4]. An inability to control or determine the equivalence ratio during most small-scale toxicity tests or to allow for its effects on toxic product yields in engineering calculations can therefore lead to considerable variability in estimations of toxic product yields and toxic fire hazard [1,7].

The most important asphyxiant gases leading to incapacitation and death in fires are CO and HCN [1]. Their yields from different materials, under different combustion conditions, depend upon the elemental composition of the fuel (carbon and nitrogen mass fractions) and the efficiency with which these elements are converted to CO and HCN in the fire effluent. Conversion efficiencies (normalized yields) for different fuels in fires cannot be predicted with any degree of certainty, so must be determined experimentally under a range of defined combustion conditions, in order to provide a database of toxic product conversion efficiencies and yields for input to engineering calculations and fire hazard assessments.

While no bench scale test can re-create exactly the decomposition conditions in a full-scale fire, the BS 7990 [8] (ISO/TS 19700 [9]) tube furnace method [7] has been developed specifically to overcome some of the problems of existing tests by decomposing materials under a range of non-flaming and flaming combustion conditions. A key feature of the test method is that the test material in strip form is introduced

into a tube furnace at a constant rate under a stream of air, providing control over the equivalence ratio and hence the combustion conditions. The furnace system provides two main reaction zones, firstly the flame zone, where pyrolysed fuel mixes with air and primary combustion takes place, and secondly the heated plume zone, where the effluent/air mixture downstream of the flame zone passes through the heated furnace tube enabling secondary reactions to occur [7].

In previously reported results, the tube furnace has been shown to produce clear sigmoid relationships between CO yields and equivalence ratios under flaming combustion conditions for a number of fuels, and a good correlation has been demonstrated between CO yields and equivalence ratios in the tube furnace and in large-scale fire experiments [2,10]. In this paper, data are presented on the relationship between equivalence ratios and HCN yields (and conversion efficiencies) for ten nitrogen-containing materials and products commonly used in buildings and building contents. Large-scale fire tests were also carried out under well-ventilated and vitiated combustion conditions on three materials for comparison.

In compartment fires, vitiated combustion conditions ( $\phi > 1$ ) can occur partly due to insufficient fresh air being entrained into the lower part of a fuel rich fire plume, or by recirculation of oxygen-depleted upper-layer products into a fire plume. The standard operating method for the tube-furnace involves passing air over the burning fuel, but to investigate the effect of combustion in oxygen depleted air a number of experiments were carried out using air-nitrogen mixtures. The effects of different furnace temperatures on HCN yields were also investigated.

## MATERIALS AND METHODS

### Materials

Table 1 shows the elemental compositions of the materials and products. These included individual polymers: polyamide 6 (PA 6), homogeneous and multi-layered products: combustion modified high resilience flexible polyurethane foam (CMHR foam), polyisocyanurate insulation foam (PIR) - faced with aluminium foil, medium density fibreboard (MDF – both untreated and fire-retarded), a boucle mixed fibre fabric (acrylic/ wool/ polyester 38 / 38 / 24), with and without a fire retardant back-coating, a velour mixed fibre fabric (acrylic/ cotton/ polyester 52 / 31 / 17), and an acrylic jersey fabric (>85% polyacrylonitrile). For the fabrics, the main acrylic component is polyacrylonitrile (~85%), with the balance methyl acrylate or methyl methacrylate. Elemental compositions were obtained by a combination of different methods depending upon the material, including calculations from elemental composition, analysis following bomb calorimetry and high temperature tube furnace runs at 900°C to provide complete specimen combustion.

Table 1. Composition of test materials.

Material	Stoich O <sub>2</sub> Demand	Elemental composition (%)							
		g/g	C	H	O	N	Cl	Br	P
CMHR polyurethane foam- FR	1.87	56.45	7.67	24.1	8.22	2.53	-	-	-
Polyisocyanurate (PIR) rigid foam	1.87	63.5	4.98	21.8	6.15	3.56	-	-	-
Polyamide 6 (PA6) granules	2.33	63.68	9.79	14.14	12.4	-	-	-	-
MDF board	1.35	47.90	6.13	41.66	3.69	0.62	<0.5	<0.01	-
MDF- FR board	1.25	45.1	5.77	39.22	6.73	-	2.66	0.63	-
Acrylic/ wool/ polyester 38 / 38 / 24 boucle mixed fibre fabric	2.02	63.1	6.4	16.7	12.89	<0.3	<0.5	-	0.94
Acrylic/ wool/ polyester 38 / 38 / 24 boucle fabric – FR back-coated	1.91	59.0	6.3	16.1	10.83	0.95	6.09	-	0.76
Acrylic/ cotton/ polyester 52 / 31 / 17 velour mixed fibrefabric	2.00	64.4	6.39	18.45	11.55	<0.3	<0.5	-	-
Polyacrylonitrile (>85%) Jersey fabric	2.33	65.62	5.71	-	23.24	-	-	-	-
Plywood	1.24	49.5	6.1	43.98	0.32	-	-	-	-

## Tube furnace experiments

The tube furnace apparatus and experimental method were carried essentially as described in BS 7990 [8]. A sample of material in the form of a strip is introduced into a tube furnace at a constant rate. A current of air is passed through the furnace over the specimen to support combustion. The effluent is expelled from the tube furnace into a mixing and measurement chamber, where it is diluted with secondary air. The effluent is then exhausted to waste. The decomposition conditions in the furnace are set using different combinations of temperature and air flow in separate runs, to model the decomposition conditions in a range of stages and types of fires as required. The aim for each experiment is to obtain stable flaming conditions for at least five minutes during an experimental run to enable measurements to be made of the composition of the effluent in the mixing and measurement chamber. The yields of each toxic product, and equivalence ratio under which the combustion was carried out were calculated from the data obtained, enabling the relationships between toxic product yields and equivalence ratio to be investigated.

For these experiments a test specimen mass of 25-50 mg/mm was used and air-flows were varied between 2 and 13 l/min in order to cover the range of combustion conditions (equivalence ratios) required. For each test run the specimen was spread evenly along the furnace boat in granular or pellet format, or as short segments. Experiments were conducted under constant steady flaming conditions (verified by observation) at a furnace temperature of 650°C. For two materials (PIR and MDF-FR) an increased furnace temperature of 700°C was required to obtain steady flaming. Additional experimental conditions for some experiments included a temperature (850°C) and the use of 10% or 12% oxygen/nitrogen mixtures instead of air. The combustion products were diluted to a standard 50 l.min<sup>-1</sup>, and sampled from the mixing and measurement chamber, where other parameters were measured. Data available include fuel mass loss, heat of combustion, smoke optical density, yields of toxic species (CO, HCN, NO<sub>x</sub> particulates etc.), and O<sub>2</sub> depletion. Further data on total airborne unburned fuel content and total unburned hydrocarbons, were obtained by further oxidation of the diluted fire effluent using a small secondary oxidizing tube furnace at 900°C, with measurement of CO, CO<sub>2</sub> and O<sub>2</sub>. Analysis of CO<sub>2</sub> and CO was by NDIR, and O<sub>2</sub> by paramagnetism (all dry) from both mixing chamber and secondary furnace. Analysis of NO and NO<sub>2</sub> was by chemiluminescence, HCN, HCl, and HBr by spectrophotometric or chromatographic analysis of bubbler solutions, smoke obscuration by optical density and particulates by gravimetry using glass fibre filters, all from the mixing chamber only.

Experiments were set up to provide nominal equivalence ratios between 0.5 and 2.5 using appropriate fuel/air ratios calculated from the stoichiometric oxygen demand for complete combustion of the entire material under test. After each run, the actual equivalence ratio achieved was calculated from the total oxygen consumed for complete combustion of the airborne fuel products in the secondary furnace (basically a phi meter method), summed with that calculated for oxidation of the particulate sample (soot) to give the total oxygen required for combustion of the airborne fuel during the sample period. The  $\phi$  value achieved was given by:

$$\phi = \frac{O_2 \text{ required } \%}{O_2 \text{ supplied } \%} \quad (1)$$

Where:

O<sub>2</sub> supplied % = ambient concentration and assumed to be 20.95%.

O<sub>2</sub> required % = the total oxygen depletion required for complete combustion of the fully oxidized fuel products released in the furnace.

For materials undergoing complete combustion, the actual phi values obtained were very close to the nominal values, but for materials forming a carbonaceous char, a proportion of the fuel was unavailable for gas phase combustion, so that the actual phi values calculated from oxygen depletion were lower than the nominal values, although very close to nominal values calculated assuming that residues were 100% carbon

## Experiments using half-scale ISO 9705 room-corridor rig

The rig was specially constructed with the “room” having dimensions ½ those of the ISO 9705 calorimeter. (Fig. 1) The corridor (4.8m long) contained a horizontal partition along its full length to prevent mixing (and secondary combustion) of incoming air with outgoing fuel-rich fire effluent. The rig was constructed from “Supalux” heat resistant mineral board panels on a wooden frame, and lagged internally with ceramic blanket (room ceiling) and externally with PIR foam panels to minimise heat losses.

The wall at the corridor end of the room rig was fitted with an adjustable sliding panel (height 1.2m) which opened to a maximum width of 30cm for maximum ventilation conditions. Fuels tested were MDF board

Table 2. Rig dimensions.

Component		length (m)	width (m)	height (m)
Room compartment		1.8	1.2	1.2
Corridor		4.8	0.6	1.2
Corridor section	upper section, effluent exit	-	0.59	0.74
	lower section, air inlet	-	0.59	0.45

and PIR foam cribs (mass 4-5 kg), placed in the centre of the room on a layer bricks to allow ventilation at the base. The MDF cribs consisted of 120 sticks 25 x 2 x 1.22 cm in 12 layers 29.5 cm high. The PIR cribs used 159 sticks 60 x 3.8 x 3.8 cm in 16 layers 63 cm high. Fire ventilation was controlled by varying the “door” panel width between 2.5 and 30 cm in a series of 14 experiments. Effluent samples were taken from the fire room at a point 12 cm below the ceiling and 20 cm from the back and side walls, and also from the upper corridor (see Fig. 1). Continuous samples were taken for CO<sub>2</sub>, CO and O<sub>2</sub>, in the fire room and corridor, with bubbler samples for HCN and grab samples (in Tedlar bags) for measurement of total hydrocarbons and total airborne fuel, taken during periods of steady-state combustion. The total airborne fuel and total oxygen demand were measured by passing a bag sample through the secondary oxidising furnace (diluting the sample with additional air if necessary), and used for calculation of the equivalence ratio under which atmosphere samples were formed using Eq.1.

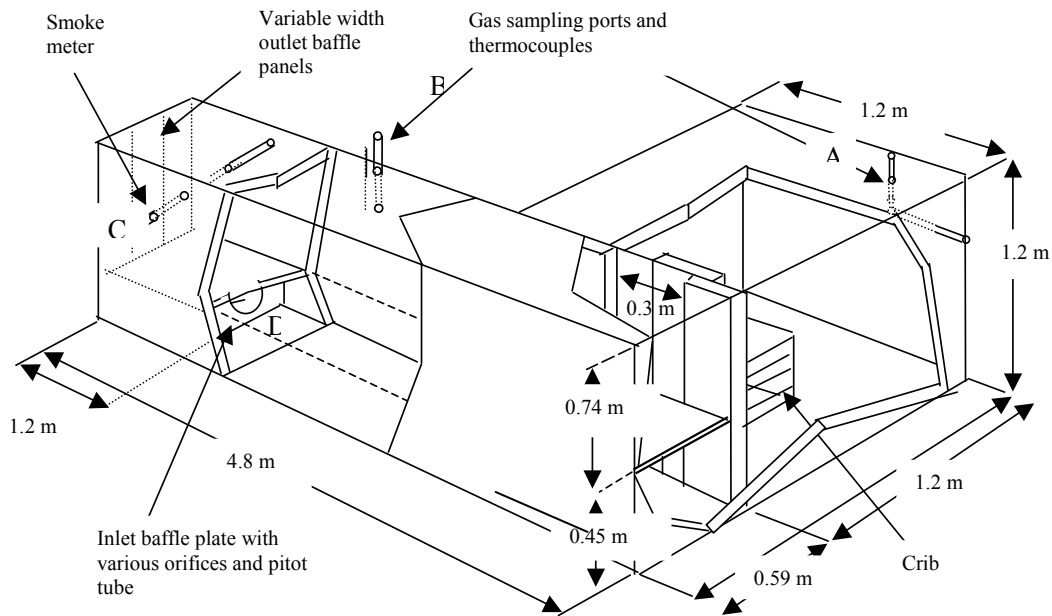


Fig. 1. Room-corridor rig

### Large-scale experiments using ISO 9705 room

For ISO 9705 room experiments, the walls were lined with MDF board or PIR aluminum foil-faced panels. The standard propane burner was replaced by MDF (16 kg) or PIR cribs (2.07 kg) as ignition sources, designed to provide a heat release rate of 300 kW. Different ventilation conditions were achieved by reducing the door width from 800mm to 400, 280 and 200mm, resulting in 50, 35 and 25% of full ventilation. To obtain large-scale yield data, fire parameters were measured in the upper layer inside the ISO room (0.4 m from ceiling and 1.0m from the from the door end of the room). Grab samples were taken using Tedlar bags, bubblers and glass fibre filters. Data were also captured in the calorimeter duct in the standard manner. Bag samples for estimation of fuel gases and equivalence ratios were taken as far as possible during periods of steady-state combustion. Equivalence ratios were calculated using the oxygen depletion method as for the room-corridor experiments.

## RESULTS

### Overall range of HCN yields in tube-furnace from all materials under all combustion conditions

Figure 2 illustrates the full range of cyanide yields (g HCN/gram polymer mass loss) obtained in the tube furnace from all ten materials and products under steady flaming decomposition conditions plotted against the equivalence ratio ( $\phi$ ). The figure shows all materials combusted in air at a furnace temperature of 650°C, (700°C for PIR and MDF-FR). Additional points are shown for some materials tested at 850°C in air, and at 650°C or 850°C under nitrogen/air mixtures containing 10% or 12% oxygen.

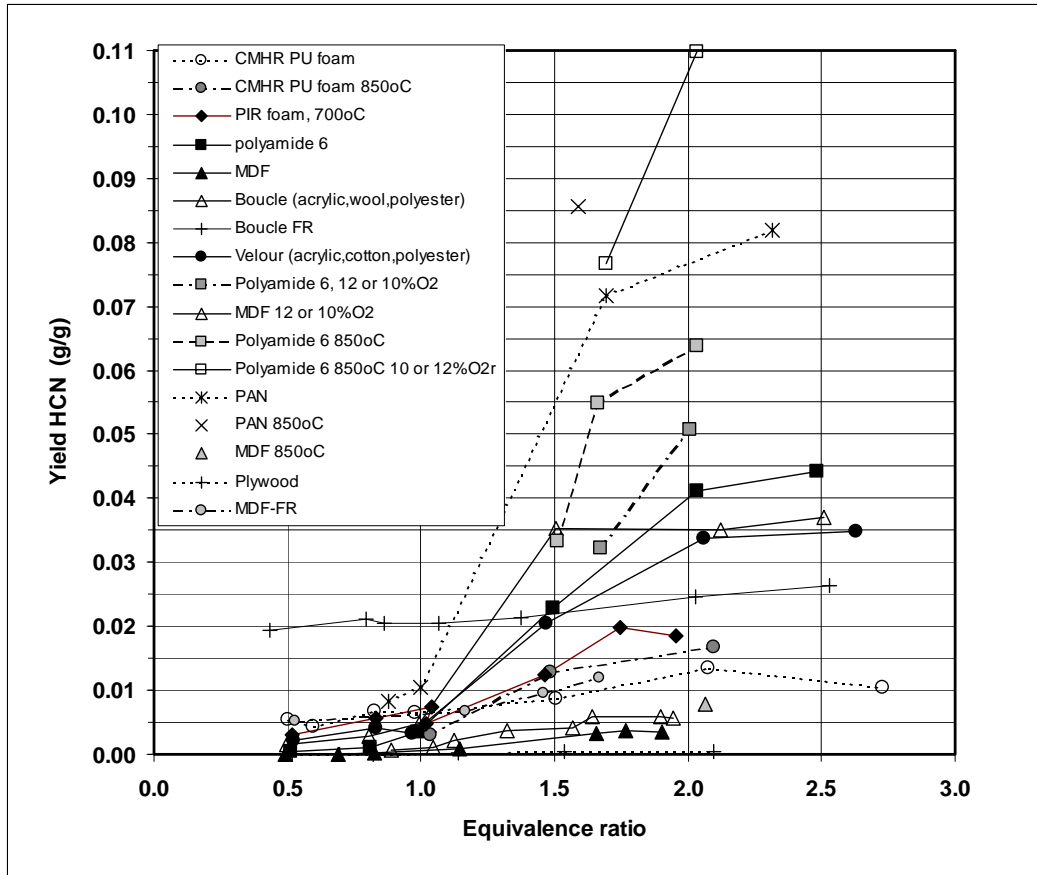


Fig. 2. Relationship between HCN yield (g HCN/g mass loss) and equivalence ratio for all materials and products under all combustion conditions in the tube furnace

For all materials except two (the boucle FR fabric and MDF-FR), there was a sigmoid relationship between equivalence ratio and HCN yield, with very low yields obtained under well-ventilated combustion conditions at  $\phi$  values  $<1$  and a rapid increase under vitiated combustion conditions, generally leveling out somewhat at  $\phi$  values above approximately 2. Yields under well-ventilated conditions were higher for materials containing halogenated, fire-retardants, compared to non-halogenated materials (so for boucle-FR fabric, the HCN yield was 13 times that of the non-FR fabric at  $\phi$  0.5).

Yields from different materials under vitiated combustion in air at 650/700°C showed a considerable range from the lowest (MDF - yield around 0.0035 g/g at  $\phi$  2.0), to the highest Polyacrylonitrile [PAN] (yield around 0.078 g/g at a  $\phi$  2.0) (excluding plywood which had a very low nitrogen content). Yields from some materials increased with temperature or low oxygen concentration (or to both), while other materials were found to be insensitive to these variables. Polyamide 6, was most sensitive to both, producing the highest yields from all materials at 850°C under 10% oxygen (Maximum HCN yield 0.11 g/g).

### Conversion efficiencies of fuel nitrogen to HCN

The wide range of yields from different materials shown in Fig. 2 means that many different functions would be required for the relationships between equivalence ratio and yields for all different materials for

engineering calculation purposes. A major variable contributing to differences in HCN yields between materials is the nitrogen content (see Table 1). If the data are expressed in terms of normalized yields, ie. conversion efficiency (fraction of fuel nitrogen in material decomposed recovered as nitrogen in the form of HCN), then differences between materials are reduced and it is possible to provide more generic functions for engineering purposes, covering groups of materials with similar decomposition behavior. Normalizing yields also enables different fuels to be compared on a common basis, so that any differences in the conversions efficiencies of fuel nitrogen to HCN between materials are revealed.

Normalized HCN yields (HCN recovery fractions) for the test materials are shown in Fig. 3. All materials except the heavily fire retarded boucle-FR and MDF-FR, show sigmoid relationships between phi and HCN recovery, with very low yields under well-ventilated combustion conditions. At higher phi levels the materials fall into two main groups, those with recovery fractions at phi levels above 1.5 increasing to a high maximum of around 0.2 in air at 650/700°C, (polyamide 6, polyacrylonitrile and acrylic mixtures, and polyisocyanurate foam), and those with lower maximum recovery fractions of around 0.1 (combustion modified flexible polyurethane foam) and 0.05 (medium density fibreboard). In order to provide generic functions for possible engineering use, and to facilitate comparison between materials in Fig. 3, a generic sigmoid expression for HCN recovery ( $F_{HCN}$ ) against phi for the tube furnace data (other than for Boucle-FR and MDF-FR) using the Weibull function, is given by:

$$F_{HCN} = k_1 - (1 - e^{-(\phi k_2 / \beta)^\alpha}) / k_3 \quad (2)$$

A single curve has been fitted to the averaged values for the high recovery group, and individual curves for MDF and CMFR foam, the very high yields from polyamide 6 at 850°C in 10% oxygen, and a linear expression for boucle-FR. Values for constants in Eq. 2 for all curves are given in Table 3.

Table 3. Generic HCN recovery fraction expressions for all materials

HCN recovery expression	$\alpha$	$\beta$	$k_1$	$k_2$	$k_3$
Polyamide 10% oxygen 850°C	15	16.5	0.003	10.1	2.2
High recovery group (most polymers)	4.5	19	0.010	12.6	6.45
MDF	4.5	16.5	-0.001	12.6	12.5
CMHR polyurethane foam	4.0	15	0.035	8.0	16
Boucle FR (acrylic,cotton,polyester) (linear)	Slope: 0.017		Intercept: 0.0827		

The relationship between equivalence ratio and HCN yields (g HCN/g fuel mass loss) for any fuel can be obtained by multiplying the recovery fraction function (or any individual recovery fraction value) by the mass fraction of nitrogen in the fuel (from the nitrogen percentages shown in Table 1) and a constant as follows:

$$Y_{HCN} = 1.928 f_{N_{fuel}} Y_{N_{norm}} \quad (3)$$

where:

$Y_{HCN}$  = g HCN/g fuel mass loss

$f_{N_{fuel}}$  = mass fraction of nitrogen in fuel

$Y_{N_{norm}}$  = normalized yield: mass or fuel nitrogen recovered as nitrogen in cyanide

The separate sections in Fig. 3 show data sets for the recovery fraction in air at 650°C (700°C for PIR and MDF-FR) and additional data points for some materials for effects of air-nitrogen mixtures (10% or 12% oxygen) or elevated temperatures. Data sets for CO recovery fraction are also plotted for comparison, and the Weibull curve for the high recovery group (Weibull Av). For each material or material group, the main variables were the extent to which there was a significant recovery at low equivalence ratios, the recovery fraction at higher equivalence ratios, and the sensitivity to lowered oxygen. The HCN recovery fraction at low equivalence ratios was higher when fire-retardant additives were present (PIR,CMHR-foam, boucle-FR and MDF-FR) but negligible otherwise (i.e. for polyamide, PAN, acrylic mixtures, and MDF). Polyamide-6 showed a maximum recovery fraction in air of 0.186, increasing to 0.212 in 10% oxygen, 0.267 at 850°C in air and 0.459 at 850°C in 10% oxygen. PAN and CMHR foam also showed some increased recovery with elevated temperature but PIR was insensitive to both increased temperature and 10% oxygen. The two fabric mixtures both contained 52% polyacrylonitrile, mixed in the boucle fabric with polyester and wool,

and in the velour fabric with polyester and cotton. At 650°C in air the HCN recoveries were very similar to that from PAN, with very slightly lower maximum recoveries of around 0.15.

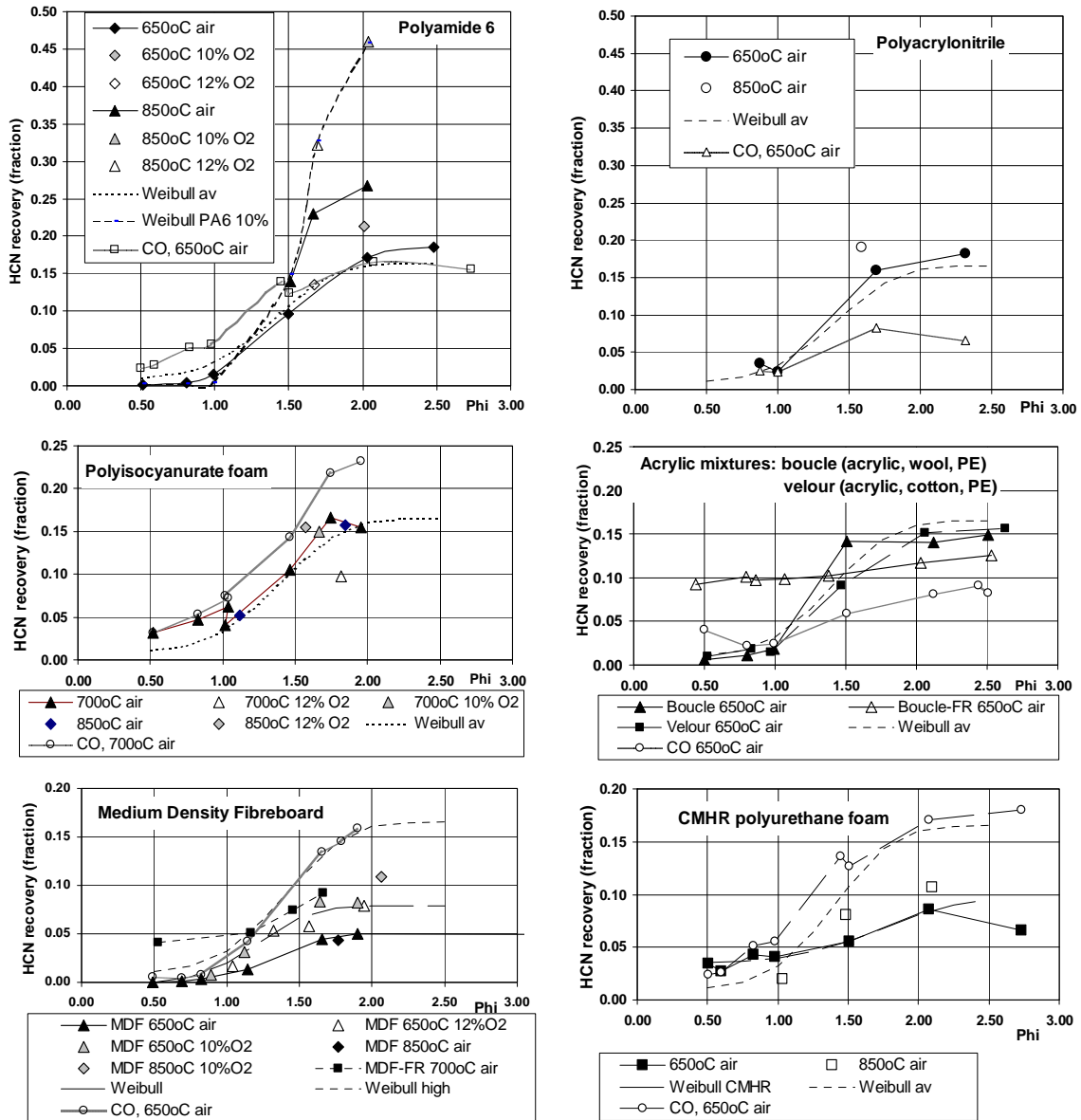


Fig. 3. Recoveries of HCN from fuel nitrogen and CO from fuel carbon for six materials and products

Both fabrics were also obtained in a fire-retarded form, with back-coatings containing brominated fire retardants. For the boucle-FR fabric it was possible to obtain steady flaming combustion conditions, but not for the velour-FR. The results illustrated in Fig 3. show high HCN recoveries of around 0.1 under well-ventilated combustion conditions at phi values between 0.5 and 1.0, with only a slight further increase under vitiated combustion conditions.

For MDF, the HCN recovery was sensitive to the oxygen concentration, with HCN recovery increasing progressively at phi values above 1.0 as the oxygen concentration is lowered. Figure 3 shows a series of points for MDF combusted in air, 12% oxygen and 10% oxygen. With 10% oxygen the recovery is increased by a factor of approximately 1.7 compared to that in air, with a maximum of 0.083. Increasing the furnace temperature to 850°C had no effect in air, but some effect in 10% oxygen, producing a maximum HCN recovery of 0.109 at a phi of 2.06. The Weibull curve is fitted to the 10% O<sub>2</sub> data. The

fire-retardant treated MDF showed elevated HCN recoveries throughout the range of combustion conditions, with a minimum of 0.04 at a phi of 0.5, increasing to 0.093 at a phi of 1.5.

### Effects of fire retardant additives on conversion efficiencies

Under well-ventilated combustion conditions, the recovery of fuel nitrogen as HCN was approximately proportional to the mass of chlorine and/or bromine content of the polymer (or bromine and phosphorus for MDF), irrespective of polymer type, as illustrated in Fig. 4. for phi 0.5. This relationship did not show at high phi levels (Fig. 4 phi 1.5), where vitiation was the main driver of HCN recovery, so that under vitiated

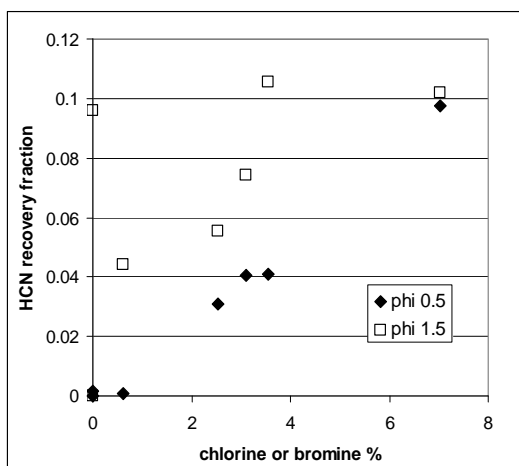


Fig. 4. Relationship between chlorine or bromine content and HCN recovery for all polymers

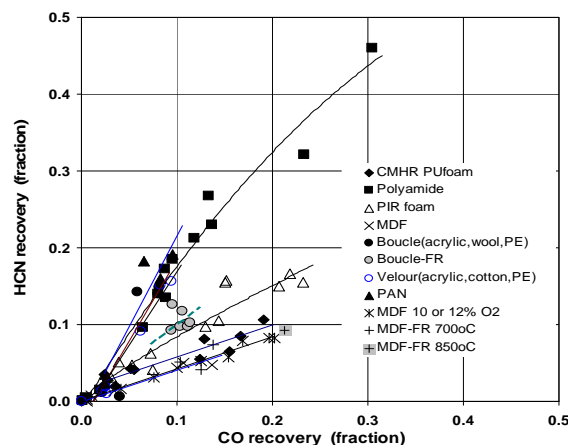


Fig. 5. Relationship between efficiency of conversion of fuel carbon to CO and fuel nitrogen to HCN

combustion conditions, the HCN recoveries were similar from the fire-retarded and untreated products for those tested in both forms (boucle fabric and MDF).

### Comparison between HCN and CO conversion efficiencies

Figure 3 shows that that the relationships between phi and normalized yields for HCN in air were similar to those for CO (some with lower and some higher recoveries). Figure 5 shows a comparison between HCN and CO normalized yields across the phi range for nine materials tested in the tube furnace. The results show an approximate 1:1 relationship for the PIR foam and the Boucle FR fabric. For polyacrylonitrile and the fabrics containing it (boucle and velour), the ratio is slightly greater than 1:1 in favour of cyanide, while for flexible PU foam and MDF it is somewhat lower.

### Comparison between HCN yields from the tube furnace and large-scale fire experiments

For two products (MDF and PIR) combustion product yields were measured under a range of combustion conditions for comparison with the tube-furnace data. For one set of experiments, an ISO 9705 room was used, with cribs and wall linings constructed from the test product. For the other set, the half-scale room corridor rig was used with the fuel in the form of a crib. In all experiments, the combustion conditions were controlled by varying the width of the fire compartment doorway. The aim in each case was to obtain a plateau period of steady flaming for each test at different global equivalence ratios depending upon the ventilation conditions. In practice this was achieved with reasonable success, but the conditions in the large-scale fires were (not surprisingly) more variable than those in the bench-scale tests, and a particular area of uncertainty arose regarding the true equivalence ratios occurring during the formation of the fire atmosphere samples taken. In the tube furnace experiments, the effluent from combustion at phi values above stoichiometric were found to contain virtually no oxygen, while the samples taken from the large-scale fire effluent, even under very vitiated combustion conditions, were found to contain some oxygen (between 0.4% and 4.5%). This oxygen may have been present in the combustion zone at the point where the combustion products were formed, or it had may have been entrained into the upper layer beyond the combustion zone and therefore merely represented a dilution of the products with secondarily entrained air. It is known from the room corridor experiments that significant post-combustion air entrainment occurred inside the fire room but beyond the combustion zone, from measurements of CO<sub>2</sub> and O<sub>2</sub> in the upper part of the divided corridor compared with those in the room, indicating a “short circuit” of air entering the



room at low level being entrained into the high level effluent plume without reaching the combustion zone. For this reason two values of  $\phi$  were calculated for each large-scale sample, comprising a “minimum  $\phi$ ” for which it was assumed that any oxygen present in the sample had been mixed with fuel in the combustion zone and a “maximum  $\phi$ ” for which it was assumed that all oxygen present in a sample had been entrained beyond the combustion zone. The range of uncertainties is illustrated in Fig. 6 in the form of “error” bars around the mean value.

Published data on HCN yields from polyamide 66 are available from the ISO 9705 pool fire experiments of Blomqvist and Lonnermark [11]. These were compared with the tube furnace for polyamide 6.

Figure 6a compares the HCN yields obtained from the large-scale ISO 9705 tests, the half-scale ISO 9705 room-corridor tests and the tube-furnace for PIR foam. The PIR was supplied as wall panels covered on two faces by aluminium foil. In the 9705 tests the cribs, constructed from PIR “sticks” cut from the panel material, burned rapidly, but the panels lining the room were virtually undamaged. The resulting fires therefore all involved a small fuel load burning in a relatively large volume of air, even with the room doorway almost closed (12.5% ventilation). The fires were well-ventilated with minimum  $\phi$  values in the range 0.26-0.5 (maximum estimates 0.46-0.80). The data form a cluster of points as shown in Fig. 6, where they are plotted as mean  $\phi$  estimates with the ranges shown as “error” bars. The data sit closely to the plotted tube-furnace data for  $\phi$  values of less than 1.0. For the room-corridor experiments, a wider range of more vitiated conditions was obtained. The data show some scatter but generally fit around the tube-furnace data, with an overall trend for increasing HCN yield with increasing  $\phi$  for all large-scale fires. The room-corridor data do show some variability, with a high yield outlier (0.026 g/g at  $\phi$  1.22 and a low yield outlier (0.009 g/g at  $\phi$  1.95). The tube-furnace HCN yields were relatively insensitive to furnace temperature and oxygen concentration.

Figure 6b shows the tube-furnace data for polyamide 6, compared to the ISO 9705 polyamide 6.6 pool fire results of Blomqvist and Lonnermark [11]. The large-scale fire test results show low HCN under well-ventilated combustion conditions, but a very steep increase in yields at  $\phi$  values between 1.0 and 1.19. The tube furnace data obtained under well-ventilated combustion condition agree closely with the large-scale data, but at the standard decomposition temperature of 650°C, the slope of the increasing HCN yield with  $\phi$  is somewhat shallow compared with the large-scale data. However, the recovery of fuel nitrogen as HCN from polyamide 6 was found to be very sensitive to both furnace temperature and oxygen concentration. The yield data from high temperature, low oxygen furnace tests are consistent with the large-scale data. Blomqvist et al. also compared tube furnace yields [12] for polyamide 6.6 with their large-scale data, obtaining a good agreement between the two methods up to  $\phi$  values of around 1.5.

Figures 6c and 6d show the tube-furnace data for MDF compared with the half-scale ISO room-corridor data and the ISO 9705 room data. The recovery of fuel nitrogen as HCN in the tube furnace was found to be low, and since the fuel nitrogen content was also low, the HCN yields were very low. However, under vitiated combustion conditions the HCN recoveries and yields were found to be somewhat sensitive to oxygen concentration as well as to  $\phi$ , so that at  $\phi$  values approaching 2.0, the HCN yield in 10% oxygen was significantly higher (around 0.006 g/g) than in air (around 0.0036 g/g). If the same variability occurs at large-scale, it is to be predicted that large-scale HCN yields for any given  $\phi$  value above 1.0 would lie between the tube furnace curves for 10% oxygen (below which combustion was not sustained) and those in air, depending upon the specific large-scale fire conditions. In practice, the yields obtained in the room-corridor test (Fig. 6c) under well-ventilated conditions ( $\phi < 1$ ) were slightly higher than those obtained in the tube furnace, and for  $\phi > 1.0$  some points approximately followed the 10% oxygen tube curve, while others lay closer to the “air” tube furnace curve. For the ISO 9705 room experiments (Fig. 6d), the data were more variable and scattered, with no obvious relationship between  $\phi$  and HCN yield. However, with the exception of one high outlier (yield 0.059 g/g at  $\phi$  0.85), and one low outlier (yield 0.0012 at  $\phi$  1.65) the tube-furnace and ISO room data are generally comparable.

## DISCUSSION

All materials or products that were non-fire retarded (or low halogen) showed a classic sigmoid relationship between equivalence ratio and HCN yield (or HCN recovery) when combusted in the tube furnace. HCN yields under well-ventilated combustion conditions were low, in some cases increasing slightly at around

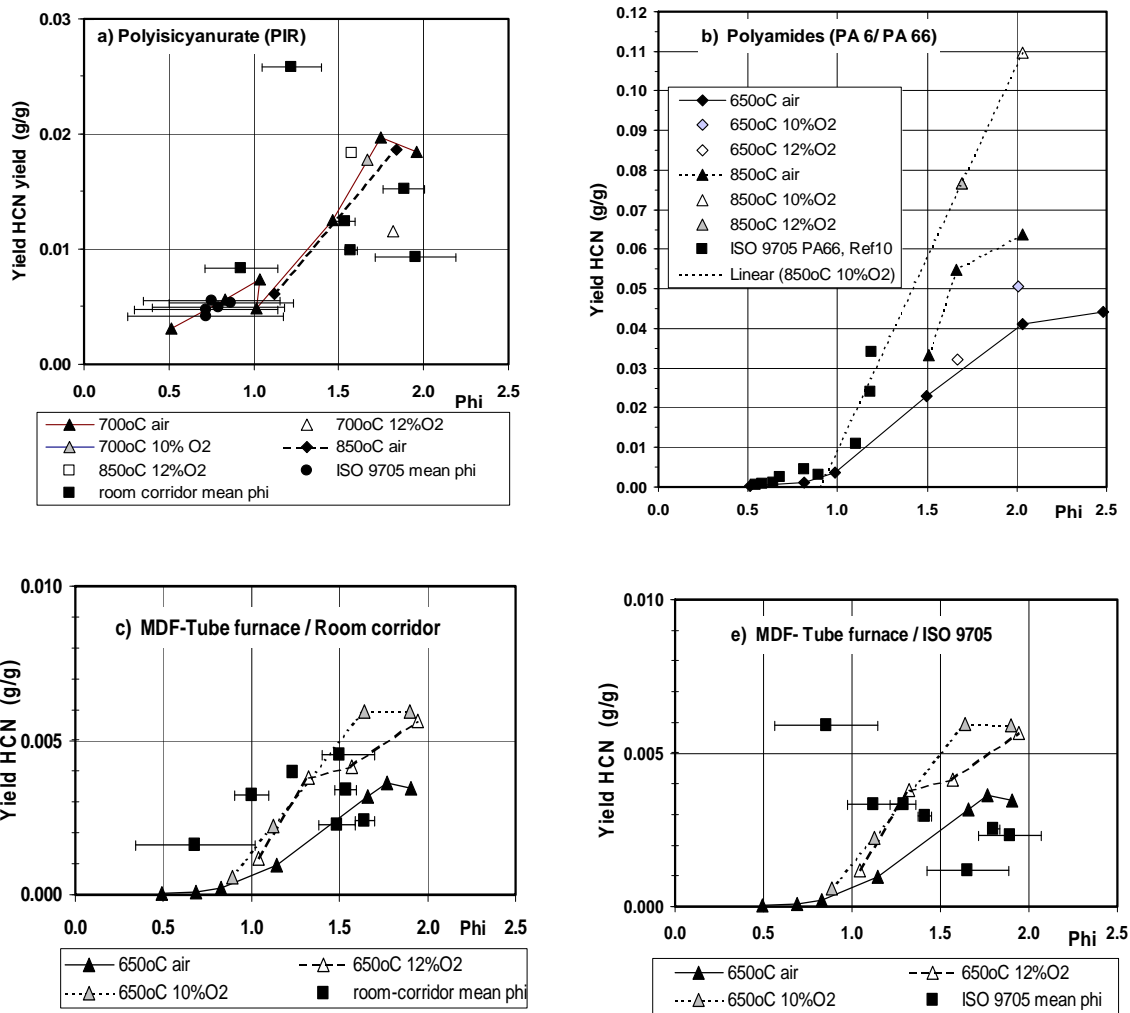


Fig. 6. Relationships between equivalence ratio and HCN yields in large-scale and tube-furnace experiments

stoichiometry ( $\phi$  1.0), then steeply increasing before levelling off at  $\phi$  values above approximately 1.5, increasing by factors of 4 -300 for different materials. This was very similar to the pattern for CO yields in the tube furnace [2,7], and also in the ASTM flammability apparatus [2,4] and in larger scale fire experiments [10]. Indeed, a generally close association has been demonstrated between the efficiency of conversion of fuel carbon to CO and of fuel nitrogen to HCN in both full-scale fires and now in the tube furnace (Figs. 3 and 5). In previous full-scale fires, it was found that for cotton and acrylic-covered polyurethane foam upholstered armchairs [13], and rigid polyurethane foam wall linings, there was an approximate 1:1 relationship between the efficiency of conversion of fuel carbon to CO and fuel nitrogen to HCN. For some fuels the relationship in the tube-furnace is close to 1:1, while others vary somewhat in favor of HCN or CO formation. Under well-ventilated combustion conditions almost all fuel carbon is oxidized to  $\text{CO}_2$ , while most fuel nitrogen is released as  $\text{N}_2$  and some oxidized to form small amounts of  $\text{NO}_x$  (mostly  $\text{NO}$  [maximum 0.0015-0.011 g/g depending on the polymer] and very little  $\text{NO}_2$ ). Under vitiated combustion conditions oxidation of both species becomes less efficient, so that a significant proportion of fuel carbon is released as CO and fuel nitrogen as HCN, other nitriles and as  $\text{NH}_3$  [11]. In experiments where nitrogen-containing materials were decomposed in argon/oxygen mixtures it has been possible to measure the production of high yields of  $\text{N}_2$  gas.

Under well-ventilated combustion conditions, the presence of halogen fire retardant additives significantly inhibits oxidation and increases the yields of both CO and HCN. This effect is illustrated in Fig. 4, which shows in increasing HCN conversion efficiency with increasing chlorine or bromine content of a fuel – irrespective of the base polymer, while for the two most heavily fire-retarded materials (the boucle-FR fabric and the MDF-FR board) the sigmoid relationship between  $\phi$  and HCN yield is almost lost, so that HCN yield is nearly constant across the  $\phi$  range.

As shown in Fig. 2, the yields of HCN from different materials under different combustion conditions varied by a factor of approximately 3000 between the lowest (non-FR materials such as MDF and polyamide 6,  $\phi < 1$ ), and the highest (polyamide 6,  $\phi 2$  at 850°C). Under vitiated flaming conditions at a  $\phi$  of 2 the range was approximately a factor of 30 between (MDF) and the highest (polyamide 6).

When normalized for fuel nitrogen content the HCN recoveries from different materials are quite similar, falling into two groups consisting of a high yield group (maximum HCN recovery around 0.16-0.2 under vitiated combustion conditions - including polyamide 6, PIR and materials containing polyacrylonitrile), and a low yield group consisting of the flexible polyurethane foam and the MDF. For flexible polyurethane foams it is known that a proportion of fuel nitrogen escapes combustion by being released into the effluent plume as an isocyanate-derived component while for rigid foams such as PIR the nitrogen is trapped in the burning solid [14].

In addition to equivalence ratio, HCN yields under vitiated combustion conditions for some materials were also sensitive to furnace temperature and/or to the oxygen concentration of air supplied, while others were less sensitive to these variables. Polyamide 6 was the most sensitive to both temperature and oxygen concentration (HCN recovery varying from 0.17-0.46), while HCN recovery for MDF was also increased in 10% oxygen. On this basis, it is predicted that for non-flashover compartment fires with upper layer temperatures up to around 600°C, HCN yields may vary somewhat depending upon the combustion environment, so that for a given global equivalence ratio in enclosed fires where deep upper layers occur, with considerable recirculation of oxygen-depleted air into the fire plume, then higher yields may occur than under conditions where fuel rich plumes entrain mainly fresh air from below. HCN yields may be increased somewhat at higher upper layer temperatures for some fuels.

### **Comparison with large-scale fires**

For polyamide 6, the tube-furnace HCN yields were compared with those obtained by Blomqvist and Lonnermark [11] when polyamide 66 was combusted as pool fires in the ISO 9705 room. Polyamide 6 and 66 are similar in composition and in other work have been found to give similar HCN yields in the tube furnace [15]. The comparison in Fig. 7 shows a very good agreement with the tube-furnace data for  $\phi$  values between 0.5 and 1.1, but the steeply increasing large-scale yields above this value are most consistent with the yields obtained in the tube furnace at high temperatures in low oxygen environments, which may better reflect the combustion conditions in those experiments.

For experiments conducted on PIR and MDF at  $\phi$  values  $>1.0$ , there was relatively little oxygen in the samples from the rear of the room in the room-corridor rig, so that the differences between  $\phi$  estimates (assuming any sample oxygen was entrained post-combustion or not) are relatively small. For  $\phi$  values  $<1$  the differences are larger, and it is likely that the true values are closer to the average or minimum.

For PIR, the tube-furnace relationship between  $\phi$  and HCN yield provides a good predictor of the large-scale results given the inherent variability of large-scale data. For MDF the HCN yields are all very low, reflecting the low nitrogen content of the fuel. The half-scale room-corridor data showed a similar relationship between  $\phi$  and yield to those from the tube furnace, albeit with more scatter. For the ISO 9705 room the HCN yields from MDF varied around the tube-furnace data set with no obvious relationship between  $\phi$  and HCN yield. One reason for this may be that the nitrogen in the fuel is not released evenly as the fuel burns, but that more is given off during the early stages of the fire. For the highly vitiated fires, samples were taken when the fire had reached near steady-state conditions, while for the better ventilated (50% door opening) fires, the samples had to be taken earlier, which may have contributed to the spread of data obtained. Taking the average for vitiated combustion conditions ( $\phi >1$ ), the average  $\phi$  is approximately 1.5 and the average HCN yield is 0.0023 g/g. This compares with a predicted value from the tube furnace data for a  $\phi$  of 1.5 at 0.0027 g/g (in air) or 0.004 g/g (using nitrogen-air mixtures), which are reasonably similar. A further complication with the ISO 9705 experiments is that, since the walls were

lined with MDF, different combustion conditions occurred in different areas of the rig (under varying equivalence ratios). Using a crib alone (as in the room-corridor experiments) or a pool fire (as in [11]), provide better large-scale models for comparison with the tube furnace data.

## CONCLUSIONS

In the tube furnace, yields of HCN, like those of CO, show a sigmoid relationship with equivalence ratio, increasing by approximately 1-2 orders of magnitude between well ventilated and vitiated combustion conditions, with considerable variation between different nitrogen-containing materials. The same relationship was demonstrated in large-scale and half-scale compartment fires, showing a good agreement, and validating the tube-furnace results. Yields normalized for nitrogen content were relatively similar between materials, and generic expressions have been fitted, enabling yields for different materials to be calculated, so that this important effect to be considered in toxic hazard assessments.

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