Test methods for smoke toxicity classification of fire-exposed construction products

Technical document

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List of abbreviations

CACC	Controlled atmosphere cone calorimeter
CIT	Conventional Index of Toxicity
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CPD	Construction Products Directive
CPR	Construction Products Regulation
FEC	Fractional Effective Concentration
FED	Fractional Effective Dose
$FIPEC_{Horizontal}$	Fire Performance of Electric Cables, Horizontal reference scenario
FSE	Fire Safety Engineering
HCN	Hydrogen Cyanide
H_2O	Water
ISO	International Organisation for Standardisation
LDPE	Low-density polyethylene (also known as polythene®)
PA	Polyamide (also known as Nylon)
PMMA	Polymethylmethacrylate
PP	Polypropylene
PVC	Polyvinyl Chloride
SBI	Single Burning Item
SDC	Smoke Density Chamber
SSTF	Steady State Tube Furnace

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1. Introduction

The European Commission is aware of the importance of the toxic hazard presented by the burning of building products. In 2016, a study was mandated to evaluate the need to regulate the toxicity of smoke produced by construction products in fires.

In January 2018, the European Commission published the final report of this study[1]. The report states that "clear definition of terminology is lacking" and "the type and format of data collected varies across Member States, and, at present, statistics on smoke toxicity are not collected and therefore the effectiveness of potential measures cannot be assessed." It concluded that "The potential dangers of smoke in general, including toxic smoke, leaking into or being generated in areas that are considered to be safe zones and/or escape routes need to be considered in new or amended existing regulations." Several fire incidents in Europe have shown that inhalation of toxic smoke represents a significant hazard for peoples' safety and is a major cause of death and injuries in fires. Recognising the need to address this life-threatening hazard, the European Commission report stated that "if the case for regulation were proven, then an agreed European system for testing and classification, with regulations and requirements at national level is favoured."

Our earlier report[2] demonstrated that classification criteria for the hazard presented by toxic fire effluent could be readily defined by combining the existing Construction Product Regulation (CPR) reference scenario, the ISO 9705 room corner test, with a gas analysis method (ISO 16405). The experimental data would yield gas concentrations as a function of time from which the fire toxicity parameters Fractional Effective Dose (FED) and Fractional Effective Concentration (FEC) could be calculated. From the FED and FEC, a material-IC_{50} (the mass of material per cubic metre to produce an incapacitating smoke and prevent the escape of 50% of the exposed group) can be used as a test-independent smoke toxicity parameter. It can be used in combination with the existing Euroclassification, A1 to E, to predict the toxic hazard of a fire. The process has a direct correspondence with that currently used for the CPR reaction-to-fire classification criteria. Once established, these reference scenario criteria would be fixed and not product dependent.

Product classification is in principle made using intermediate-scale tests which are validated by their demonstrated correlation to the reference scenario[3] and complementary small-scale experiments. The purpose of this document is to identify a process, covering all product types to demonstrate compliance with defined classification criteria. The development of classification test methods is the domain of technical groups such as CEN/CENELEC, and this report does not seek to promote particular test methods. For reaction to fire classification, several test procedures are in use for different types of product and classes of fire behaviour. Similar flexibility may need to be employed for toxicity hazard assessment. However, for a given type of product and class of fire behaviour, a single, consistent method would need to be defined. This report provides a review of alternative smoke toxicity test methods and

the results that have been obtained from them. The report considers test conditions, sample definition, treatment of data and correlation with the reference scenario.

2. Effect of Fire Conditions on Smoke Toxicity

The intrinsic smoke toxicity of a material or product is a function of the following parameters, which are physically and chemically inter-connected and therefore cannot be considered individually:

2.1. Sample flammability
The toxic hazard from a burning product is its flammability (or mass loss rate) multiplied by its smoke toxicity (or toxic product yields). The smoke classification (s1, s2, s3) reported in the current CPR is based on measurements from the SBI test. Thus, a product of low flammability will not burn very much, so it will produce little smoke even if the yield of smoke is high when it is reported on a "per g of mass loss" basis. Similarly, smoke toxicity should be reported on the same mass used in the test (or mass-charge) basis.

2.2. The presence or absence of a flame
Flames involve very rapid chemical reactions; thus, the presence or absence of a flame will profoundly affect the smoke toxicity. Typically, flaming combustion reduces the smoke toxicity by up to one order of magnitude[4], but the presence of a flame significantly increases the fire growth rate.

2.3. Thermal conditions
The temperature development in a compartment fire and the different stages of the fire influence the toxic yields of products (see Section 4, Figure 7). Figure 1 presents an idealized variation of the temperature development in a fire compartment along with the different fire stages.

In addition to the fire load in the compartment and the ventilation conditions, the fire behaviour of materials and products will also determine the temperature development inside the fire compartment. Thus, both the modulus and the time base for the temperature curve would to a certain extent be product and/or product family dependent. **Error! Reference source not found.** illustrates a generic representation of the temperature curve based on a schematic from Troitzsch[5].

Figure 1. Idealised description of the temperature development with time in a compartment fire[6]

2.4. Ventilation conditions

For flaming combustion, the ventilation condition is the single most important parameter governing smoke toxicity. Typically, the toxicity increases between 5 and 25 times as the fire grows to be ventilation controlled (Figure 1). Ventilation condition can be defined by the oxygen concentration to the fire, and in the fire effluent; the CO/CO_2 ratio; and the equivalence ratio ϕ (the actual fuel-to-air ratio divided by the stoichiometric fuel-to-air ratio). The equivalence ratio has been shown to give the most consistent, material-independent relationship between the yields of the main asphyxiants in fire effluents, carbon monoxide (CO) and hydrogen cyanide (HCN) and the ventilation condition[7,8].

The critical feature is that all enclosure fires will become ventilation-controlled, provided there is sufficient fuel to support fire growth. This ventilation-controlled stage, where the fire cannot get enough oxygen, creates high toxic product yields which are believed to be responsible for most fire deaths[9].

In order to demonstrate correlation with the reference scenario, the toxic product yield for a particular material or construction product must be reported alongside both the test temperature and ventilation condition.

2.5. Chemical composition

Combustion is to a large extent dependent on the chemical composition of the fuel. Under ideally well-ventilated conditions, the combustion of simple materials, for example polyethylene (PE) or polypropylene (PP), will yield mostly carbon dioxide and water. As the conditions become under-ventilated, and for other more complex materials, a wider spectrum of gaseous effluents are produced. The presence of heteroelements, such as halogens, nitrogen, phosphorus and sulphur are likely to increase the smoke toxicity, while aromatic (benzenoid) rings in the main polymer chain normally reduce smoke toxicity by reducing the volatile production. However, it

is believed that out of this spectrum only a relatively small number of gases need to be considered in order to assess the acute toxic hazard[10].

Some materials are non-combustible, while others have inherently low combustibility. In some construction products, more flammable materials have combustion properties modified by the addition of flame retardants. Irrespective of whether the product has inherently low combustibility, or this is achieved by the addition of flame retardants, there are two mechanisms for reducing flammability – action in the gas phase or in the solid phase. In general, flame retardants acting in the gas phase will interfere with the formation of carbon dioxide and water, increasing the yields of many toxic products of incomplete combustion and significantly increasing the smoke toxicity. In contrast, condensed phase action, such as enhanced char formation, will reduce the amount of smoke, or gas phase effluent[11].

2.6. Sample geometry

The importance of sample geometry and end use application are acknowledged in a Position Paper by the Group of Notified Bodies[12] which requires that reference scenario data is generated from products in a realistic installation. In terms of bench scale classification testing, the use of bulky products or specific installation methods is clearly impossible due to test method size constraints. In addition, the testing in isolation of minor components, such as sealants, cable ties, fire-stopping materials, penetration seals and linear joint seals shall not be necessary. The key to resolving this issue is a demonstrated correlation with reference scenario.

3. Test methods

Reaction to fire tests are designed to assess the response of combustible materials to fire. Mostly, they have been designed to assess flammability, for which the worst-case scenario is usually the atmospheric oxygen concentration (21%). Smoke toxicity assessments are also reaction to fire tests, but in this case the worst-case scenario results from burning in significantly less oxygen, maybe 7 to 14%, where yields of most toxic products are much higher. Thus, a distinction may be drawn between test methods that have been designed specifically for the assessment of smoke toxicity, and flammability tests have been adapted to measure smoke toxicity. The initial stages of flaming in the ISO 9705 room have been shown to be adequately represented by the Single Burning Item (SBI) test EN 13823 for Euroclass A2 to D[13, 14]. The test utilises full scale product samples in different standardised configurations that represent product end-use conditions. A number of sample mounting and fixing variations to suit different products have been specified in harmonised technical specifications. In a large-scale test such as the reference scenario ISO 9705, as the fire grows, it becomes ventilation controlled, and the toxic product yields increased significantly[15]. It has not proven possible to replicate the behaviour of large-scale fires in a single bench-scale test. Some bench-scale tests attempt to replicate the entire fire growth curve (Figure 1) with a single test, while others use one test to replicate an individual fire stage.

As described in our earlier report[2], attempts have been made to use the SBI test for assessment of smoke toxicity. Unfortunately, it was unsuitable for such assessment because it can only replicate a well-ventilated fire scenario. If it were to be enclosed in a restricted ventilation chamber, this would reduce the fire growth rate, invalidating the flammability part of the test. In addition, the large air flow through the exhaust duct, necessary to ensure operator safety, means that for many less-flammable products, the toxic gases in the exhaust duct are below the detection limit of most analysers.

It is therefore necessary to evaluate alternative fire test methods that can be used to evaluate the smoke toxicity of construction products. An extensive experimental evaluation of fire toxicity test methods has been conducted by the Research Institute of Sweden (RISE)[16].

The fire test methods described below have been considered as possible test methods to evaluate smoke toxicity, outlining their strengths and weaknesses.

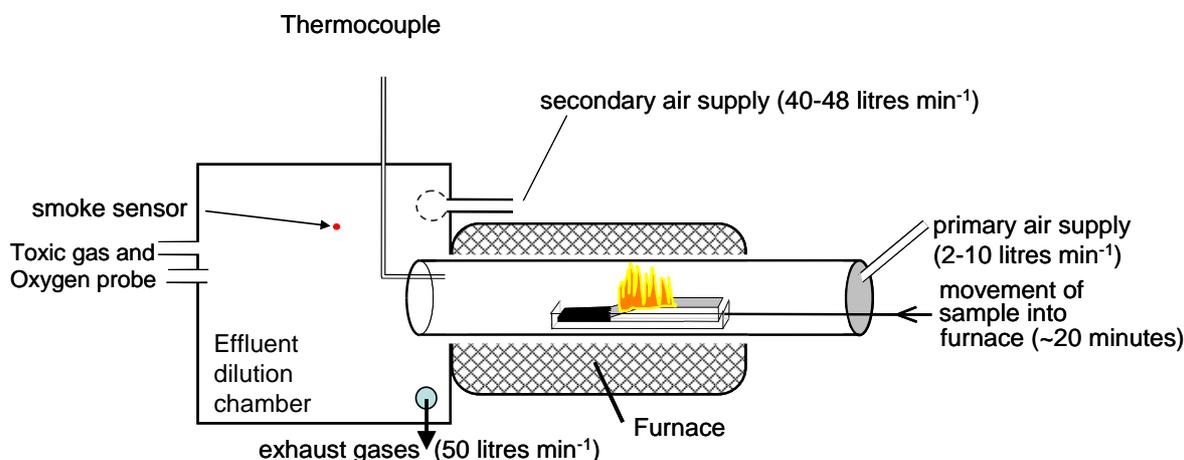### 3.1. Steady State Tube Furnace (SSTF) ISO/TS 19700
The steady state tube furnace (SSTF) is the only fire test available that was specifically designed for the assessment of smoke toxicity through its ability to replicate each fire stage by steady burning. Its development follows from the DIN 53436 toxicity standard, which uses a static sample and moving annular furnace.

Table 1 Assessment of the Steady State Tube Furnace extracted from ISO 16321-2[17]

Physical model	Fire stages*	Type of data	Apparatus assessment	Use in fire regulation	Validation of the method
ISO TS 19700 Tube furnace (BS 7990)	Oxidative pyrolysis (1.b) Well ventilated flaming (2) Under ventilated flaming (3)	• O2 concentration • Gas concentration and yield • Smoke generation • Lethality - irritancy evaluation as: Possibility to use animal	**Advantages** • Small scale replication under steady state conditions • Enable yield of toxic gases evaluation **Disadvantages** • Limited number of equipment available • Requires pretesting to obtain the desired conditions • Representativity and exposure of finished product is not accurate • Unrepeatable condition of burning • No indication of the rate of burning (do not differentiate FR and non-FR materials • No direct toxicological results correlation	None reported in the standard	No comparison of toxic potency and gas yields against real scale test data

The SSTF[18], shown in Figure 2, feeds the linearly uniform sample into its hot zone at a fixed rate, under a controlled air supply, inside a horizontal silica tube of diameter 48 mm, allowing adequate mixing of fuel and oxidant. It forces combustion by driving the sample into a furnace of increasing heat flux at a fixed rate, so that, by running several tests with the same material with different ventilation conditions, each fire stage can be replicated by steady state burning. The products generated in the flame zone then pass through the heated furnace tube, maintaining a high temperature, as they would in the upper layer of a compartment fire. After an initial peak corresponding to spontaneous ignition, the toxic product yields may be quantified from the gas concentrations and mass feed rate during the steady state burn period. It has been designed to generate data for input to fire hazard assessments, using the methodology in ISO 13344[19] and ISO 13571[20], particularly in relation to the ISO fire stages[21]. Linear or particulate samples are distributed evenly in a long silica boat over a length of 800 mm which is fed into a tube furnace at a typical rate of 1 g min^{-1} with a controlled flow of primary air. Secondary air is added and mixed in the effluent dilution chamber to give a total gas flow through the apparatus of 50 L min^{-1}. The conditions in the middle of the steady-state tube furnace were measured at temperatures of 650 and 825 °C, giving a heat flux of 39 and 78 kW m^{-2} respectively[22].

Figure 2 The steady state tube furnace apparatus, ISO TS 19700.

By driving a sample at a fixed rate into a ventilation-controlled furnace where the heat flux increases as it moves into the furnace, the apparatus forces combustion under the full range of fire conditions, including ISO fire stages[21]:

1b Oxidative pyrolysis

2 Well-ventilated flaming

3a Small, under-ventilated flaming

3b Large, under-ventilated flaming (post-flashover)

Toxic product yields can be quantified from a combination of mass feed rate and gas concentrations during steady burning which can be correlated to a specific fire condition, from the temperature and ventilation data. Products such as HCN, CO, CO_2, NO_x and acid gases can be accurately quantified. Ventilation conditions can be quantified both as equivalence ratio and as CO/CO_2 ratio. The equivalence ratio can be obtained directly from the results (as described in ISO TS 19700), even for products of unknown composition. In addition, mass balances, such as carbon balances, allow a reality check on the data, ensuring that all reported data are self-consistent.

A detailed interlaboratory reproducibility study (ILRS) has been published[23] on the ISO/TS 19700 steady state tube furnace, demonstrating a high degree of reproducibility. Samples of different polymers (PMMA, LDPE, PA6.6 and rigid PVC) were tested under two fire conditions:

- Well-ventilated flaming at 650 °C
- Post-flashover under-ventilated flaming at 825 °C

Each laboratory performed three replicate runs on each polymer under each condition. The results showed good agreement between laboratories and against calculated stoichiometric maxima, demonstrating satisfactory levels of repeatability and reproducibility for key combustion gases. These included O_2 consumption, and the

yields of CO_2, CO, HCN and HCl. A further ILRS is currently being undertaken using a wider range of materials/products.

The test apparatus is currently available as a commercial apparatus from at least one European manufacturer of fire test equipment[24].

3.2. Fire Propagation Apparatus (FPA), ISO 12136

The Fire Propagation Apparatus (FPA)[25] shown in Figure 3 contains the fire zone in a vertical cylindrical silica tube where the fuel is able to mix well with the oxidant while avoiding contact with the heaters which are external to the tube. These external heaters expose the material (typically a 100 mm x 100 mm plaque of up to 25 mm in thickness) to thermal radiation with ignition from a pilot flame.
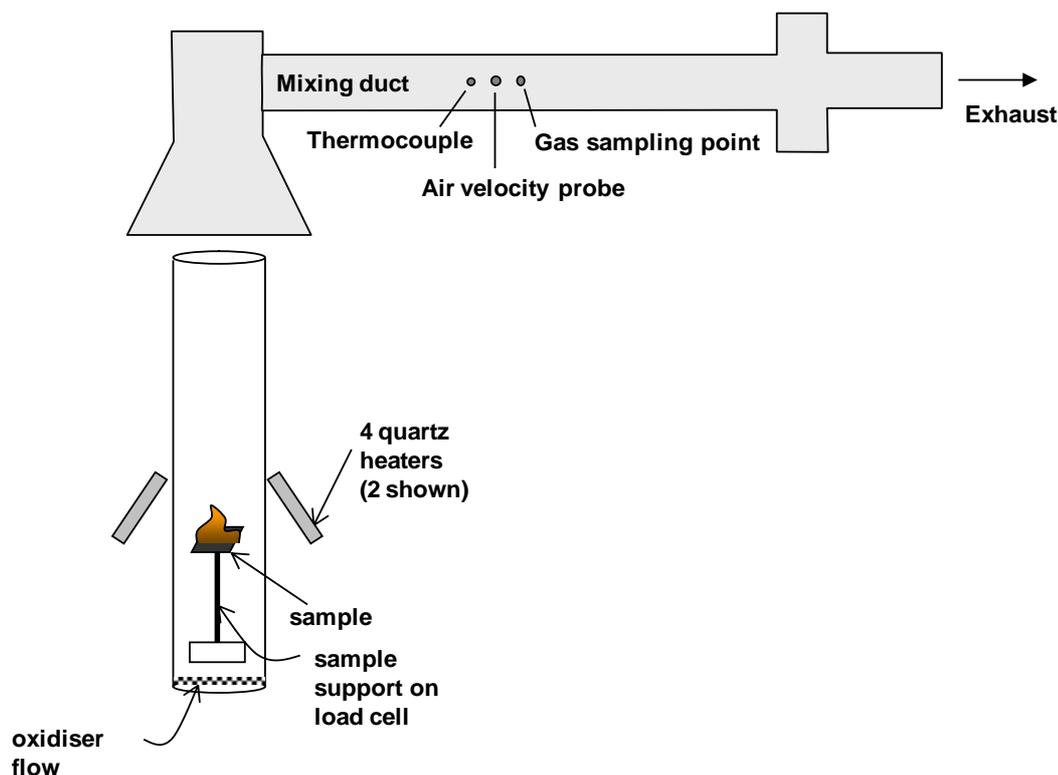
Figure 3 The fire propagation apparatus (ISO 12136)

Throughout the test, the following are monitored:

- Sample mass
- CO and CO_2 generation
- Oxygen consumption (to measure heat release rate)

This enables the calculation of the rate of heat release and fuel-to-air ratio, allowing the fire stage to be identified.

Table 2 Assessment of the Fire Propagation Apparatus extracted from ISO 16321-2[17]

Physical model	Fire stages*	Type of data	Apparatus assessment	Use in fire regulation	Validation of the method
Flame propagation apparatus (ISO 12136, NFPA 287 and ASTM E 2058)	Oxidative pyrolysis (1.b) atmosphere: Anaerobic pyrolysis (1.c) Well ventilated flaming (2) Under ventilated flaming (3)	• Mass loss • Gas concentration • Gas yield • Smoke obscuration • Exhaust gas vitiation	Advantages • Representativity and exposure of finished product is accurate • Long experience on the method • Control of fuel/air equivalence ratio • Measurement of mass loss rate • No contact between fire effluents and heater • Link with fire development possible • CO yield correlate with real scale Disadvantages • Correlation with real scale only available for CO not for other gases • Limited number of equipment available • No attempt to evaluate toxicity data	None identified in the standard	No inter laboratory trial reported Validation against real scale test only available for CO

The test has previously been used for the quantification of toxic product generation, with published data describing the yields of CO and hydrocarbon production[26], as a function of ventilation condition, expressed as equivalence ratio, showing fairly good agreement with large scale test data. It is, however, an expensive apparatus and only products available in a suitable (flat panel) geometry can be tested.

Repeatability and reproducibility of the Fire Propagation Apparatus (FPA) is accepted but limited to its use as a method for assessment of flammability, heat release, and smoke.

It is commercially available from at least one European manufacturer[27].

3.3. Controlled Atmosphere Cone Calorimeter (CACC), Not standardised.

The Cone Calorimeter (ISO 5660) is a widely used, well-ventilated fire test apparatus. Without modification, the Cone Calorimeter is able to replicate early well-ventilated flaming where the small flaming fire would typically generate the minimum amount of toxic products.

Table 3 Assessment of the Cone Calorimeter extracted from ISO 16321-2[17]

Physical model	Fire stages*	Type of data	Apparatus assessment	Use in fire regulation	Validation of the method
Cone calorimeter (ISO 5660-1, ATSM E 1354, NFPA 271, NFPA 272)	Oxidative pyrolysis (1.b) Well ventilated flaming (2) With controlled atmosphere: Anaerobic pyrolysis (1.c) Small, localised fire (3.a) Post flash over fire (3.b)	• Mass loss • Gas concentration • Gas yield • Smoke obscuration • Exhaust gas vitiation	**Advantages** • Representativity and exposure of finished product is accurate • Widely available • Toxic potency data linked to heat release • Enable direct use of yield data for FSE • Heat release rate and smoke data correlated with real scale tests **Disadvantages** • Highly over ventilated - link to real scale especially post flashover difficult • ISO 5660-Part 5: reduced oxygen atmosphere - condition between pyrolysis and combustion may be different - Post combustion may occur but can be reduced by adding a chimney • Fraction of air flow through the combustion zone is unknown: uncertainty of global equivalence ratio • Effluents passing through the radiant heater leading to possible modification • Gases produced highly diluted	None identified in the standard	Low level of correlation with real scale in term of toxic potency and gas yield. Method not assessed against real scale test for oxidative pyrolysis and well ventilated flaming

In order to replicate the behaviour of developed, ventilation-controlled fires, a series of non-standardised modifications have been made to the apparatus, including enclosing the combustion zone, providing controlled ventilation into the chamber, and lengthening the effluent ducting.

This has led to the development of a variety of Controlled Atmosphere Cone Calorimeters (CACC) shown schematically in Figure 4. The modifications help the apparatus to replicate oxygen depleted conditions as the enclosed chamber allows for the control of the air-flow within the chamber, while an elongated effluent duct helps to simulate the conditions of a reactive upper layer.
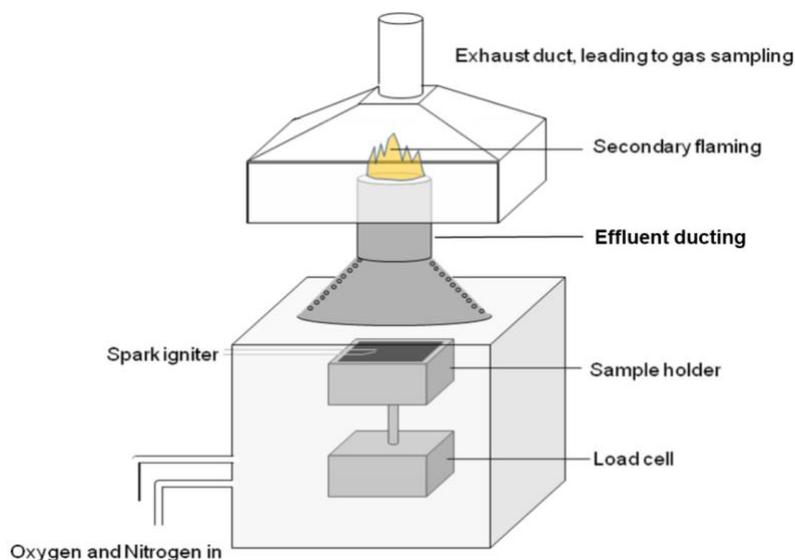
Figure 4 The controlled atmosphere cone calorimeter

Early laboratory tests on an apparatus without an elongated effluent duct have shown[28] that the fire effluent produced tends to continue to burn as it emerges from the chamber, resulting in well-ventilated secondary flaming occurring outside the chamber due to the amount of oxygen required for combustion exceeding the amount fed into the enclosed chamber. To minimise this, an elongated effluent duct (≈1m) has been added, preventing mixing with air until the effluent had cooled sufficiently, while allowing time for under-ventilated plume reactions to go to completion. When the longer duct is used, better agreement with large scale test data is obtained. When subjected to under-ventilated flaming conditions, the vaporised fuel can lift from the surface without ignition occurring, replicating the more toxic, but slower burning non-flaming condition.

The Cone Calorimeter relies on a load cell to record the instantaneous mass loss during the run. Unfortunately, in the time taken for the reduced oxygen atmosphere to stabilise before the run, the test sample becomes pre-heated to decomposition temperatures, meaning that satisfactory measurements cannot be obtained using heat fluxes above 50 kW m$_{-2}$, as the sample decomposition is too rapid, and the load cell gets too hot to provide reliable mass loss data (needed to establish yields and mass balances)[29]. The ambiguity of the combustion conditions and difficulty in defining the ventilation conditions means that the toxicity data produced does not represent a specific fire condition (see Section 2)[30]. The method also suffers from its lack of standardisation, so different apparatuses exist, perhaps with each modification solving a different problem in achieving agreement with large-scale test data.

Two reports of the use of the CACC for assessment of fire toxicity describe experimental programs investigating a range of fuels. In one, 6 materials, including PVC, polyisocyanurate foam, and a glass reinforced polyester containing brominated flame retardant are described[31], but the only results reported are the HCl yields. In

the other paper[32], some carbon monoxide yields are reported for the burning of an undefined "sandwich composite material" which shows higher CO yields (up to 0.07 g/g) in well-ventilated conditions, (the oxygen concentration was 21% and 14%), and much lower (0.03 g/g) for oxygen concentrations of 0, 5 and 9 %. Based on these results, the authors conclude that "no gas phase oxidation can occur below 10% O_2: the formation of CO tends to decrease." This is in direct contradiction of the observations from large scale fires where CO yields above 0.2 g/g are common in oxygen concentrations below 10%, presumably because burning in the CACC cannot be sustained at the applied heat flux. Indeed, upper layer oxygen concentrations as low as 1.2% O_2 have been measured[33]. It appears that there is a significant body of work necessary before the CACC can replicate the higher yields of toxic products associated with under-ventilated flaming.

The controlled atmosphere cone has been built in a variety of designs, and, as yet, no standard geometry has been established. Since the design affects the results, no assessment of interlaboratory repeatability or reproducibility have yet been possible.

It is commercially available from at least two European manufacturers[24,27]. A non-standard controlled atmosphere accessory is also available from at least one of these manufacturers.

3.4. The Smoke Density Chamber (SDC, ISO 5659-2)

The Smoke Density Chamber (SDC) shown in Figure 5, is one of the most widely used fire-test apparatuses in the world, producing data on the visual obscuration effects of smoke which are necessary to ensure safe escape. This ready availability has encouraged its historical development as a tool for smoke toxicity generation and quantification, specifically for the rail, maritime and aircraft industries[34,35,36].
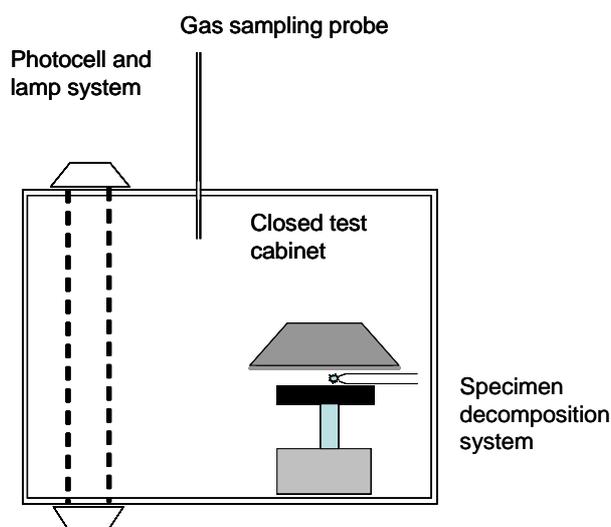
Figure 5 The smoke density chamber (ISO 5659-2) showing a sampling probe for fire smoke toxicity.

Table 4 Assessment of Smoke Chamber extracted from ISO 16321-2[17]

Physical model	Fire stages*	Type of data	Apparatus assessment	Use in fire regulation	Validation of the method
Smoke chamber (ASTM E662 ASTM E 1995 ISO 5659-2)	Oxidative Pyrolysis (1.b) and small Under - ventilated flaming combustion (3.a)	• Total mass loss • Smoke obscuration • Gas concentration of specific fire effluents (continuous or at specific time)	Advantages • Simple and widely available. • Reasonable representation of the finished product Disadvantages • Combustion condition not well characterised • Possible stratification of smoke leading to non-representative sampling of the combustion gases • Represent only one stage of fire • Difficult to monitor effect on animals	IMO (International Maritime Organisation) Aerospace: EN standards, Airbus (ABD) and Boeing (BSS) specifications	Difficult to relate to real scale scenario

ISO 5659-2 includes four different test conditions, with and without piloted ignition, at two values of constant heat flux, 25 and 50 kW m^{-2}, although these are not related to specific fire scenarios. The higher heat flux is insufficient to prevent the extinguishment of flames when oxygen levels begin to fall. In real fires, heat fluxes in excess of 50 kW m^{-2} force combustion in under-ventilated conditions. It has been shown that the smoke density chamber fails to replicate under-ventilated flaming[37], even for one of the most flammable polymers, polyethylene, attempts to force under-ventilated flaming, by increasing the mass of material used in the test led to the flame going out prematurely, with very similar asphyxiant yields to those of the well-ventilated condition[37]. This shows that the test is unable to produce the high yields of toxic gases associated with under-ventilated flaming.

In addition, the means of quantifying toxicity is also compromised by the design of the chamber:

- The single sampling point, located near the top of the chamber, leads to wide variation in gas concentrations, dependent on the movement and mixing of the smoke plume.
- Small changes in the movement of the smoke can leave the sampling point in, or out of the smoke plume.

The interlaboratory reproducibility of the Smoke Density Chamber (SDC) as a toxicity assessment tool has proved extraordinary challenging. It appears that both the toxic

gas generation, and the method of assessment of the toxic components of the smoke varied widely from laboratory to laboratory. Despite its inability to replicate under-ventilated flaming, it is used in EN 45545-2 to assess the smoke toxicity of components for railway vehicles - TRANSFEU. In combination with Fourier Transform Infrared (FTIR) gas analysis it has been approved as an ISO technical specification. The scope of ISO/TS 19021 explains why it is unsuitable for adoption as a tool for assessment of smoke toxicity by the CPR.

> "This document does not address the accuracy of this fire model for any product application, nor does it address the accuracy of the gas concentrations relative to any real-scale fire tests or fire scenarios. For future conversion of this document into an International Standard, an interlaboratory trial is intended to be conducted to replace Annex B."

> "This document does not include any toxicity assessment or provide input data for fire safety engineering."

> "As combustion conditions vary depending on the oxygen consumption rate in the enclosure during the ISO 5659-2 test, this physical fire model is not recognised as being representative of any specific fire scenario. Therefore, it is difficult to compare test results with real-scale fire conditions. As a consequence, if this test method is used for comparison among materials or products, it is intended to be done in combination with other fire tests."[38]

It is commercially available from at least two European manufacturers[24,27].

3.5. The Static Tube Furnace (NFX), (NF X 70-100)

The Static Tube Furnace (NFX) method shown in Figure 6 forces the thermal decomposition of a small static specimen in a furnace with metered airflow, driving the effluent into a sampling system. This is described in the French standard: *Tube furnace thermal degradation method*[39].
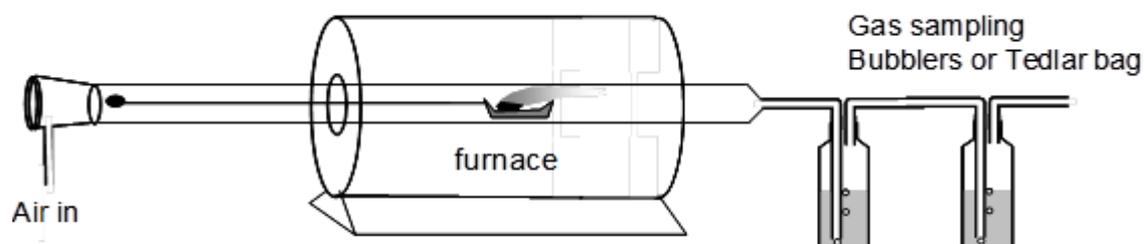
Figure 6 The static tube furnace test, NF X 70-100

The fuel-to-air ratio is not routinely determined, although this may be possible, if the rate of pyrolysis is determined using on-line analysis. The rate of pyrolysis is not only temperature and material dependent, but also a function of heat transfer to the specimen. Testing at the same sample mass and air-flow may result in fuel-to-air ratios that vary with specimen geometry, boat thickness, material and furnace temperature.

Table 5 Assessment of the static tube furnace extracted from ISO 16321-2[17]

Physical model	Fire stages*	Type of data	Apparatus assessment	Use in fire regulation	Validation of the method
(NF X 70-100; EN 45545-2; UITP E6; NATO AFAP-3)	Oxidative pyrolysis (1.b) Well ventilated flaming (2) Under ventilated flaming (3)	• Mass loss • Gas (10) concentration and yields	Advantages • Easy to use • Flexibility of operating conditions Disadvantages • Small specimen size - only homogeneous material • Combustion conditions cannot be identified easily • Multiple burns are needed to evaluate all the gases considered • Toxic potency of the product in its end use not evaluated • Sample size limited • Correlation with real scale questionable • Limitation for condensable gases • Combustion depends upon behaviour of each specimen and can change during the test; • No indication on the rate of burning	French railway European railway (limited to cables) NATO	/

The standard specifies the application of 3 different conditions, specified by furnace temperature. These conditions are not linked to a particular fire stage, however it could be roughly assumed that:

- 400°C corresponds to pyrolysis without ignition representing oxidative pyrolysis (stage 1b, provided flaming did not occur).
- 600°C corresponds to well-ventilated flaming (stage 2, provided flaming occurred).
- 800°C corresponds to under-ventilated flaming (stage 3a or 3b, provided flaming occurred), as the rate of pyrolysis will be slower at 600°C than 800°C, so the fuel-to-air ratio at 600°C will be lower.

The methods consider only a small quantity of material for the evaluation and therefore tests are performed on materials and not on products. The method has been adopted by the European rail industry as part of a toxicity assessment standard EN 45545-2. While studies on repeatability and reproducibility are available both on the combustion itself and on the chemical analysis specified in the standard, there has been no reported attempt to relate the test conditions to the stages of real fires.

The test apparatus is currently available from at least one European manufacturer of fire test equipment[24].

4. Correlation to reference scenario - TOXFIRE

There are very few studies relating the toxicity of burning materials in large-scale tests to their yields in bench-scale tests. The data set resulting from the European Commission funded TOXFIRE project[40] is one of the best large-scale data sets on smoke toxicity available. Their use of a "phi meter"[41] to measure the fuel-to-air ratio during their ISO 9705 room test[42] allowed for the fire condition to be defined in terms of fuel-to-air ratio, making it an ideal data set to be used for comparison with bench-scale test results.

The steady state tube furnace (SSTF) and the fire propagation apparatus (FPA) both show good agreement with the large-scale fire test data[37].

Figure 7 shows a comparison for the CO yield from PP as a function of equivalence ratio, using controlled atmosphere cone calorimeter data published as part of the TOXFIRE project[40], steady state tube furnace data[43], and data from the fire propagation apparatus[44] (actually reported for LDPE which is isomeric with PP), compared to the large scale data. It is apparent from all tests that the inherent variation in burning behaviour gives much larger scatter in under-ventilated conditions than in well-ventilated conditions. In general, this shows a significant increase in the CO yield as the fire moves from well-ventilated to under-ventilated. Yields from the controlled atmosphere cone calorimeter are shown as average values as a function of equivalence ratio (ϕ)[26] and corrected values of the equivalence ratio, (ϕ_{eff}) where the oxygen depletion which resulted from flaming occurring outside the enclosure, above the cone heater, detailed in reference[28], was taken into account in the equivalence ratio calculation. With a single exception, the controlled atmosphere cone calorimeter failed to replicate the higher CO yields associated with large scale behaviour.
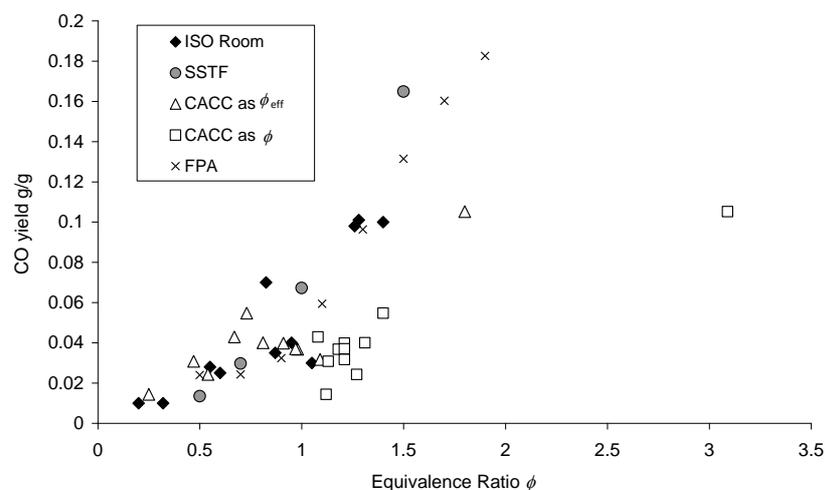
Figure 7 Comparison of CO yield for polypropylene for large scale (ISO Room), steady state tube furnace, fire propagation apparatus and controlled atmosphere cone calorimeter, as a function of equivalence ratio ϕ.

Figure 7 shows acceptable agreement between the ISO room data and the steady state tube furnace, the controlled atmosphere cone calorimeter, and fire propagation apparatus data which actually generated greater extremities of well- and under-ventilated burning than occurred in the ISO room. However, in the results from the controlled atmosphere cone calorimeter, there is only a single data point (at $\phi = 3.2$ or $\phi_{eff} = 1.8$) which shows the higher yields of carbon monoxide associated with under-ventilated combustion, suggesting that it is not easy to replicate this condition in the CACC. Data for the controlled atmosphere cone calorimeter generally shows lower CO yields in under-ventilated combustion, and after the correction for combustion outside the chamber, the apparatus is unable to replicate the more toxic conditions of under-ventilated burning responsible for most fire deaths, and therefore has limited value as a tool for assessment of fire toxicity.
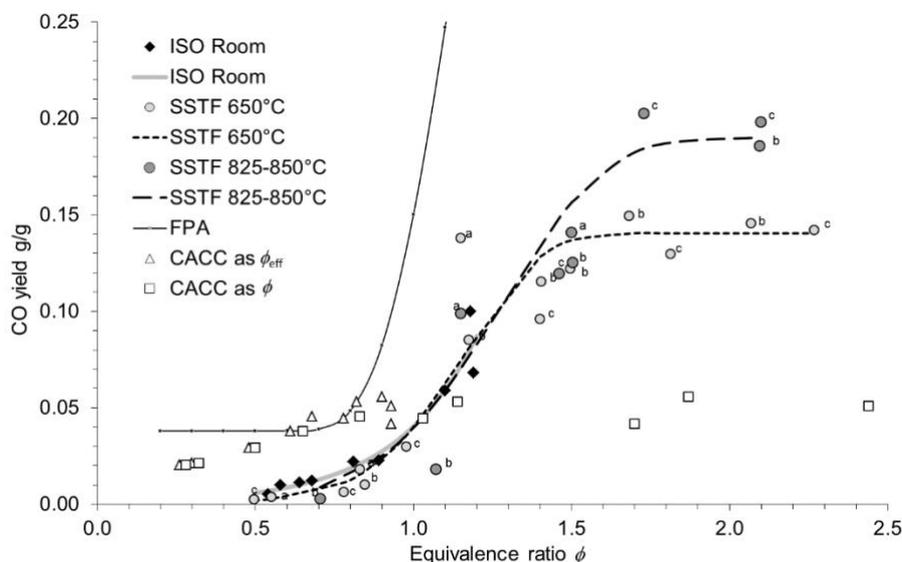
Figure 8 Comparison of CO yield for aliphatic polyamides from steady state tube furnace, controlled atmosphere cone calorimeter, fire propagation apparatus, with ISO Room, as a function of equivalence ratio ϕ Letters indicate the data source and material for SSTF: a) polyamide 6.6[45], b) polyamide 6.6[46], c) polyamide 6[47].

Figure 8 compares the published CO yields from the large scale ISO room tests, for PA 6.6 under a range of ventilation conditions with those from the controlled atmosphere cone calorimeter, steady state tube furnace[43] and the fire propagation apparatus[26]. The SSTF data include results from four data sets: a) Blomqvist[45], b) Stec[46], and c) Purser[47]. Of the three SSTF data sets, a) was obtained using the same batch of polyamide 6.6 as was used for the ISO 9705 Room in the TOXFIRE project; b) was polyamide 6.6, obtained from a different source; c) was for polyamide 6 (which has identical chemical composition and a slightly different structural formula to PA 6.6). Again, this shows a significant increase in the CO yield as the fire moves from well-ventilated to under-ventilated, accompanied by an increase in scatter, using all methods. CO yields in the SSTF were found to be temperature sensitive, with

somewhat higher yields at 825-850°C than at 650°C. During the ISO room tests at the higher equivalence ratios the upper layer temperatures were 750-1000°C, corresponding more with the higher temperature SSTF results. The SSTF results are very similar from all three aliphatic polyamide samples. It is notable that the controlled atmosphere cone calorimeter results, based on the averaged local equivalence ratio ϕ, reported by Hietaniemi[28] show higher CO yields in well-ventilated conditions and, crucially, lower CO yields in under-ventilated conditions. Again, the data have been corrected by calculation of the effective equivalence ratio ϕ_{eff} which aligns the yields to the well-ventilated stages of the large-scale data.
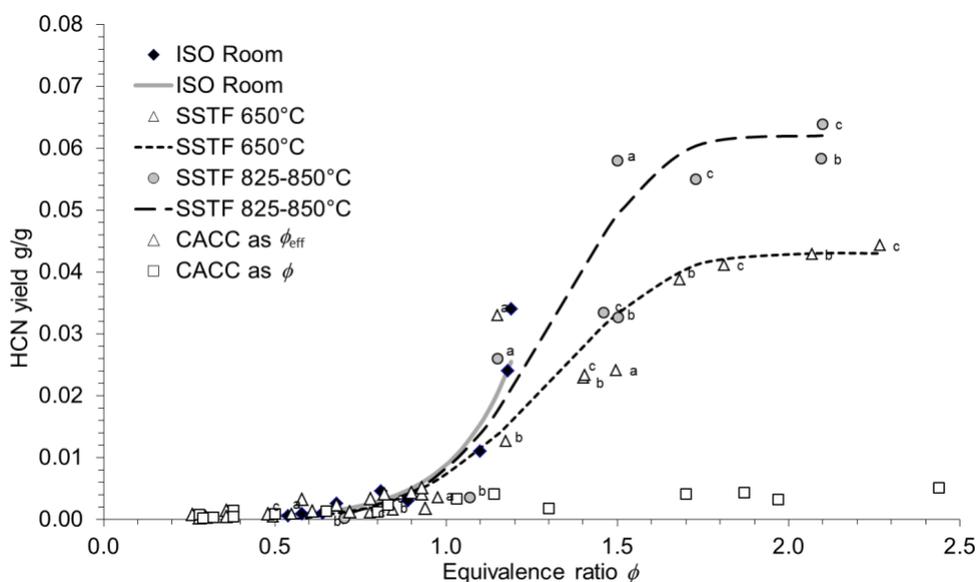
Figure 9 Comparison of HCN yield for aliphatic polyamides from steady state tube furnace and controlled atmosphere cone calorimeter with ISO Room, as a function of equivalence ratio ϕ Letters indicate the data source and material for SSTF: a) polyamide 6.6[45], b) polyamide 6.6[46], c) polyamide 6[47].

Figure 9 shows the same ISO room experiments compared for HCN yield to the steady state tube furnace, and the controlled atmosphere cone calorimeter. Again, this shows good agreement between SSTF and large scale, alongside the sensitivity of HCN yields from polyamides to the furnace temperature in under-ventilated conditions. This illustrates the failure of the controlled atmosphere cone calorimeter to replicate the conditions of under-ventilated combustion even more dramatically. While the controlled atmosphere cone calorimeter data fit well with the large-scale data up to ϕ = 1, they do not replicate the higher CO and HCN yields for under-ventilated conditions where $\phi > 1$. Unfortunately, Tewarson has not reported a similar correlation for HCN yield from PA 6.6 from the fire propagation apparatus. It is apparent that the controlled atmosphere cone calorimeter also fails to replicate the higher yields of the other major asphyxiant, hydrogen cyanide in under-ventilated fires. Indeed, the ~50-fold increase in HCN yield as the fire condition changes from well-ventilated to under-ventilated is

not seen using the CACC. Again, correcting the data to ϕ_{eff} merely compresses it to below an equivalence ratio of 1.0.

The steady state tube furnace and fire propagation apparatus can thus adequately replicate large scale burning, but the controlled atmosphere calorimeter cannot.
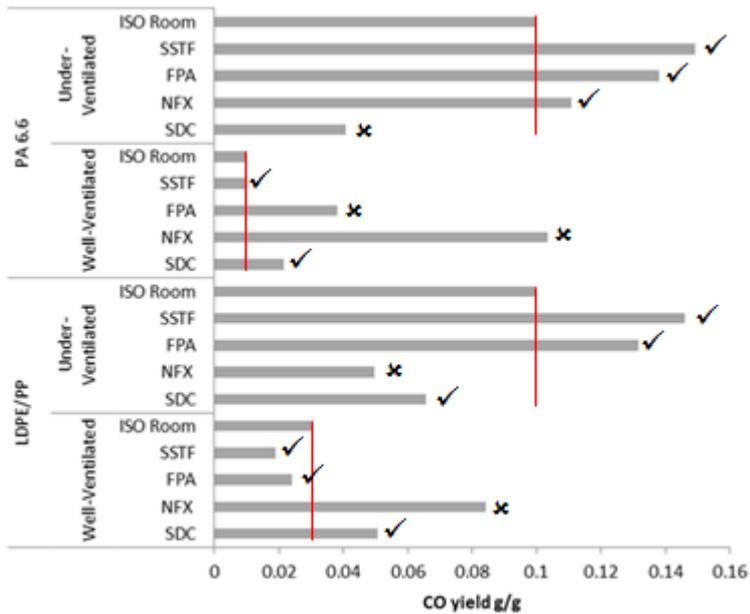
5. Comparison of methods

Difficulty in replicating the conditions of real fire conditions and behaviour arises as a result of the following practical issues:

1) The yield of toxic products is dependent on the fuel-to-air ratio; this is often indeterminate for test methods designed to assess flammability.
2) If smoke is recirculated into the flame zone, as happens in the Smoke Density Chamber, the toxicity may change.
3) Uncertainties and errors will arise in apparatuses where the fuel-to-air ratio changes, as this limits the time available for taking mass loss and effluent composition measurements, at a particular fire condition.

During a real fire, reactions occur both in the flaming zone and in the hot layer above it. To replicate this, the test apparatus must keep the effluent hot after it leaves the flame zone. To replicate under-ventilated flaming the applied heat flux must be sufficient to force burning at low oxygen concentrations. This may be best achieved by forcing the sample to burn at a fixed rate, independent of its flammability, rather than using a fixed heat flux and allowing the sample burning rate to vary.

For tests methods unable to monitor the fuel-to-air ratio, such as the SDC and NFX, assigned fire conditions were used as a means of comparing toxic product yields against large scale testing.

Figure 10 shows the comparison of CO yields obtained from different fire conditions carried out on different laboratory methods using and PA 6.6., and low-density polyethylene (LDPE) and polypropylene (PP). It has been shown that these latter two polymers (LDPE and PP), which have identical elemental composition, give indistinguishable yields of carbon monoxide as a function of ventilation condition [46].

Figure 10 Comparison of CO yields obtained from different fire conditions carried out on different laboratory methods (symbol ✓ indicates reasonable agreement with large-scale ISO Room, symbol ✶ indicates no reasonable agreement)

All tests exhibit some degree of variation, most prominently during under-ventilated conditions. However, the general trend is an exponential increase in CO yield as the fire condition transitions from well-ventilated to under-ventilated. This illustrates the smoke density chamber's (SDC) inability to produce meaningful toxicity data that is representative of large-scale fire behaviour. For under-ventilated conditions, the static tube furnace (NFX) typically underestimates the yields of CO, particularly for LDPE and PP, in addition to typically overestimating yields in well-ventilated conditions. The steady state tube furnace (SSTF) showed best agreement for LDPE/PP and PA 6.6 at well-ventilated conditions. However, compared to the ISO room it over-estimates CO yield at under-ventilated conditions both for LDP/PP and PA 6.6. The fire propagation apparatus overestimated yields of CO production for all tests with the exception of LDPE/PP at well-ventilated conditions.
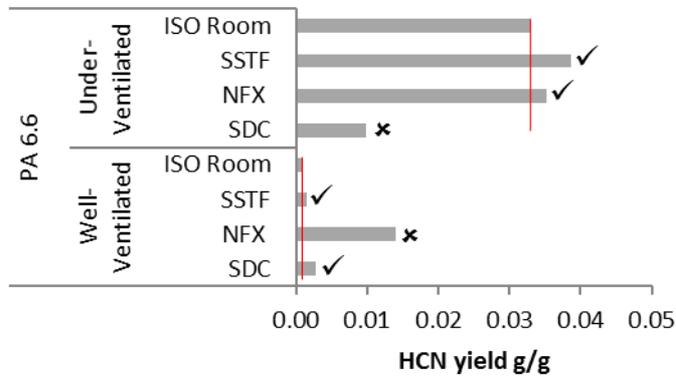
Figure 11 HCN yield in different laboratory-scale tests and fire conditions

Figure 11 compares the HCN yield for PA 6.6 in the ISO Room and SSTF in well-ventilated and under-ventilated conditions to those in the NFX and SDC tests. This also shows high HCN yields for well-ventilated conditions in the NFX test, but lower HCN yields for the SDC. In contrast, in under-ventilated conditions, the NFX test shows good agreement with the SSTF, while the SDC fails to replicate the high HCN yields associated with under-ventilated flaming.

6. Discussion

The reference scenarios underpinning the room corner test and SBI were taken as the basis, and to address smoke toxicity, the document looked at under-ventilated conditions which are important to assess the most smoke toxic conditions. In theory, any test demonstrating correlation of smoke toxicity to the defined reference scenario could be considered for product classification. In the case of less combustible products, which do not progress beyond well-ventilated flaming when tested in the ISO 9705 reference scenario, the equivalence or CO/CO_2 ratio might be relatively low and subject to detector sensitivity, the classification test (SBI) or cone calorimeter suitably instrumented might be appropriate. However, there is no evidence that either method would be suitable for products demonstrating under-ventilated combustion in the reference scenario. For simplicity and robustness, a single test method covering all degrees of combustibility remains the most attractive option.

From the limited data available, the steady state tube furnace method (SSTF) looks the most promising. Although not considered in this paper the related DIN 53436 tube furnace method might also be considered. Additionally, the experimental evaluation of fire toxicity test methods conducted by the Research Institute of Sweden (RISE) on different combustible and non-combustible products also indicates that the SSTF is the most useful test method for assessing smoke toxicity both for controlled flaming combustion and pyrolysis test with non-combustible materials. As such, the method is a useful tool that can be applied for a wide range of materials and constructions products.[16]

To limit the scope and cost of testing it is important to take advantage of available reaction to fire data. This will normally include the defined reference scenario and specific product classification data. The objective is to limit the scope of the testing by the definition of the experimental variables – temperature and ventilation. This is the work of the defined product groups who are better placed to deal with problems/anomalies specific to a given product family.

Existing Euroclass data from bomb calorimetry (EN ISO 1716), single burning item (EN 13823) and small flame ignitability test (EN ISO 11925-2) can be used to provide data on the flammability or mass loss rate. The methodology has been described elsewhere[48]. Used in combination with toxic product yields this can be used to generate material-LC_{50} values for burning in the reference scenario test.

The additional testing and classification for smoke toxicity can be applied complementary to the current classification system for reaction to fire. As smoke toxicity can be measured independently from the other fire parameters used in the Euroclass system, it is not necessary to retest and reclassify construction products already on the market. The products on the market can maintain their current classification for reaction to fire, smoke production and flaming droplets with additional testing to determine the toxicity of the smoke generated by the product.

In general building entire products are too large to be tested directly on a bench-scale. It is known that the physical form and installation will have an impact on the reaction to fire properties which is why reference scenario tests are carried out on products installed according to end use application. For smoke toxicity testing, provided the temperature and ventilation conditions of the reference scenario are respected, the actual form of the sample might be of less importance. This means that sections removed from the product or composites produced from the raw materials involved could be tested. Non-combustible components need not be considered. This approach could significantly reduce the demand for extended application testing (such as products with different dimensions, made from the same material).

The experimental data reported derives primarily from EU sponsored research and mostly concerns simple polymeric materials. There is a need to establish reference scenario data for some real products. This should include a variety of wall lining materials, one linear product (e.g. pipe insulation[i]). The products to be evaluated could be selected from those tested in the second SBI round robin and/or the recent RISE test programme. Product choice should be driven by relevance to current and future building practice. Samples should cover products with a potentially wide range of toxic hazards.

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[i] Cables are excluded as their classification is based on highly ventilated reference scenario not predicted to yield realistic toxic hazard. Furthermore, the need to use a reference scenario not based on the room corner test would have significant cost implications.

7. Recommendations

1. Any bench scale test demonstrating correlation with reference scenario data could be considered for toxicity classification.
2. For many products the potential test methods are limited to those that can generate both well-ventilated and under-ventilated data.
3. It is recommended that future test method assessment is focussed on those based on a horizontal tube furnace – SSTF, NFX or possibly the DIN furnace. From the results presented in this paper it might be concluded that the SSTF is the most promising.
4. To limit the scope and cost of toxicity classification, the test variables (temperature and ventilation) should be defined using reference scenario data from the relevant product family.
5. Prior elemental analysis of a material can reduce the need for toxic gas quantification.
6. There is a need to establish reference scenario toxicity data for some real products. This will enable toxicity classification criteria to be confirmed and the proposed classification test methods to be evaluated.

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