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TOXFIRE – Fire Characteristics and Smoke Gas Analyses in Under-ventilated Large-scale Combustion Experiments

Abstract

In the CEC project Guidelines for Management of Fires in Chemical Warehouses, TOXFIRE (EV5V-CT93-0275), carried out by a consortium of seven European partners, SP Swedish National Testing and Research Institute has carried out controlled large-scale combustion experiments on amounts in the 100 kg range.

A set of indoor, controlled large-scale combustion experiments was performed on materials with different chemical composition. The degree of ventilation (global equivalence ratio) was varied from well ventilated to under-ventilated, and determined with a phi meter that measures the amount of additional oxygen required to achieve complete combustion. In addition to measuring the traditional fire-related parameters, extensive chemical characterizations of the smoke gases were carried out. Two series of tests were performed, where both the scale and the experimental configuration were varied.

This report summarises the results and compares the results from the two tests series with data from experiments performed in smaller scales by other partners within the TOXFIRE projects. Comparisons are also made with large-scale free-burning well-ventilated experiments.

It has been shown that it is possible to attain under-ventilated conditions on a scale as large as that in the ISO 9705 room. Further, larger-scale fires such as those in the storage configuration facility do not appear to alter the outcome of the combustions significantly. The ISO 9705 room scale can hence be taken as a model for real-scale fires, at least as long as modestly complex systems in space are studied.

Contents

Foreword

1 Introduction

In most countries there are large numbers of chemical plants and storage facilities that handle and store substantial amounts of hazardous substances, *e.g.* pesticides. Fires involving chemicals seem to be one of the more important hazards from these activities. Today, only limited documentation is available concerning the assessment of the potential consequences from fires at chemical plants and chemical storage facilities.

The project *Guidelines for Management of Fires in Chemical Warehouses* (TOXFIRE) was initiated in order to remedy some of these problems. The project, financially supported by the CEC ENVIRONMENT programme (contract no. EV5V-CT93-0275), was carried out by an international consortium during a three years period (1993-1996) including the following partners:

- Risø National Laboratory, Denmark (co-ordinator; Risø)
- NERI – Danish National Environmental Research Institute
- South Bank University, United Kingdom (SBU)
- VTT – Technical Research Centre of Finland
- Lund University, Sweden (LU)
- SP – Swedish National Testing and Research Institute
- FOA – Swedish National Defence Research Establishment

The main objective of the TOXFIRE project was to provide the basis for guidelines to be used by fire engineers and fire brigades when dealing with fires in chemicals. Numerous accidents have shown that lack of knowledge and information is the most important reason for the severe damage to environment and humans normally resulting from fires in chemicals. Systematic preplanning around various types of incidents, including fires, will increase the possibilities considerably of eliminating risks or reduce their consequences. The effects of an accident would then be a sequence of events along an anticipated path with a set of defined options for the required emergency activities. In order to achieve this a lot of structured information is needed.

Considerable effort was put into combustion experiments to provide various inputs for the guidelines. Fires in chemicals were carried out in scales from about 10 g to 100 kg in order to demonstrate how large a combustion experiment is required to yield information valid in guidelines concerned with real scale fires in chemicals. The largest-scale combustions were carried out at SP.

This report summarises the SP work. More detailed information on the various parts of the SP work is given in references 1 through 5. The TOXFIRE project in its entirety is reported on in reference 6.

2   TOXFIRE – Project structure

The central core of prevention is an assessment of risk for the specific activities at the facility in question as shown in Figure 1. This requires numerous specific inputs, such as *e.g.* information about the chemicals involved and their behaviour in various types of fires. The structure in Figure 1 describes the overall structure of the TOXFIRE project intended to cover the essential parts needed for a risk assessment and provide the basis for relevant guidelines.

Classification of substances and materials is a central input in the risk assessment structure. The aim is to identify the types of chemicals of interest and put them into groups of common chemical composition and structure, behaviour when heated, etc. Based on a number of source characteristics, substances are classified in terms of ignitability, heat release, burning rate, smoke evolution, combustion products, survival fractions and the influence of packaging materials on the combustion products. In the TOXFIRE project the source characteristics were described by parameters obtained from combustion experiments at various scale and by analysing the effects of scaling.
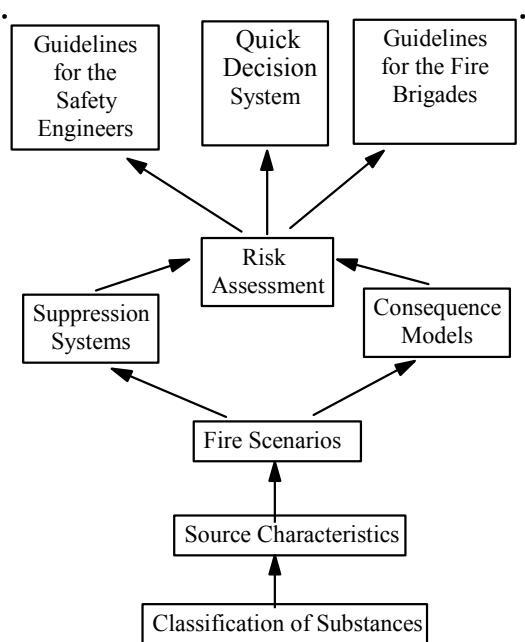
Figure 2.1   Structure of the TOXFIRE project, reflecting the information required for risk assessment.

The combustion products are normally given as yield values, defined as production of a certain product per mass of fuel loss, and the heat release as effective heat of combustion, *i.e.* the amount of heat produced in a fire per mass of fuel lost. These parameters will be effected by the degree of ventilation (under-ventilated, stoichiometric or well ventilated conditions). Generally, it is hardly possible to determine these parameters in full-scale tests and relevant small scale testing must be utilised. The possible scaling effects and their influence on yield values and effective heat of combustion were among the main issues in the TOXFIRE project.

Determinations of the source characteristics comprise the principal experimental work. Combustion experiments were conducted in various scales and under various ventilation conditions by Risø [7, 8] (micro-scale), VTT [9] (cone-calorimeter scale), LU [10] (medium- scale) and SP (large-scale). Determinations of dioxin formation in the different scales were made by NERI [11] and the analysis of the scaling effects has been carried out by LU [12].

The fire scenario is likewise important in the risk assessment. It has a direct influence on the choice and dimensioning of the fire suppression system or fire brigade action. It also has an immediate influence on the consequences, both regarding the direct fire damage to the facility and the more indirect damage to humans and the environment.

The ventilation conditions in all scales are, of course, related to various fire scenarios. Advanced modelling is required to determine the consequences from a given fire scenario. Several models are needed, firstly to estimate the fire development inside the building and the response of suppression actions. In the TOXFIRE project a model describing the influence on stored materials was developed by SBU [13]. Further, models are required to determine the smoke gas dispersion from the fire and following that, the effects to humans and the environment. This work was conducted by FOA [14-17], VTT [18] and SBU [19].

In order to make the information accessible for fire safety engineers and fire brigades, there is a need for informative guidelines, in relation to *e.g.* fires in chemical warehouses. They could form the basis for the preventative measures and the tactical planning of a fire fighting operation, respectively. In the TOXFIRE project, the basis for these two sets of guideline documents was developed. In parallel, the core for a quick decision system to be used by the fire chief in case of chemical fire was developed. Risø [19], VTT [20], LU [21] and FOA [22] carried out this work.

An overview of the TOXFIRE project and a full listing of all reports and documents is presented by Petersen and Markert [6]. An overall summary of how the various input data could be applied in the planning of fire prevention and fire protection to manage fires in chemical warehouses is described by Rasmussen [20]. The report shows how the work made by each partner in the project is linked into the risk assessment structure with a brief overview of the work conducted by the various partners.

3 TOXFIRE – Large-scale experimental work

The responsibility of SP in the TOXFIRE project was to perform controlled large-scale fire tests at different ventilation conditions, aimed at providing source characteristics in situations that were as close to full scale fire scenarios as possible from a safety and economical point of view. These results should form the basis for the estimation of the scaling effects for testing performed in a smaller scale. The SP work is summarised in this report while a more detailed account is given in references 1 through 5, respectively.

The SP work was carried out in co-operation between the departments of Fire Technology and Chemical Analysis. Two types of experimental set-ups were used. Most of the large-scale experiments were carried out in the ISO 9705 room with the chemicals in a steel pan during the combustion experiments [1]. This test arrangement was considered to be the optimum – large enough in scale to represent full-scale conditions and, moreover, sufficiently controlled to provide good and repeatable test results. A few tests were performed in an even larger scale test enclosure, 256 m³, that was built to allow "real" storage configurations [2]. These tests were performed as a complement to the ISO 9705 room tests, to give an idea of the influence from sample configuration and room size on the fire characteristics, in particular on the nature of the products of combustion.

Five different materials were used in the large-scale tests. Great care had to be exercised in the selection of compounds since they were to be used in rather large quantities indoors and combusted under poor ventilation conditions. To obtain reasonable complexity in the composition of the smoke gases, the elemental composition, in addition to just carbon-hydrogen-oxygen, included nitrogen, sulfur and/or chlorine, respectively, in the materials selected for large-scale combustion [2]. The materials studied were polypropene (PP), Nylon 66 (Ny), tetramethylthiuram monosulfide (TMTM), 4-chloro-3-nitrobenzoic acid (CNBA), and chlorobenzene (CB).

Four individual experiments were performed in the ISO 9705 room on each of the materials. In the storage configuration test enclosure, one configured test was performed on each material, with the exception of chlorobenzene; see Section 3.2.2. In addition, two open pool combustions (polypropene; chlorobenzene) were carried out in that larger test facility.

During these tests, all the common fire test parameters were measured, such as temperature, heat release rate, smoke production rate, etc. In addition, extensive measurements were carried out to characterise the smoke gases.

3.1 Degree of ventilation

As the degree of ventilation is a decisive parameter for characterising different types of fires, it is important to be able to control it as well as to have a proper measure for it. The degree of ventilation, in principle, is the ratio of *oxygen required* over *oxygen available* for complete stoichiometric combustion. This so-called equivalence ratio, ϕ, is defined as

$$\phi = \frac{\dot{m}_{fuel} / \dot{m}_{oxygen}}{\left(\dot{m}_{fuel} / \dot{m}_{oxygen}\right)_{stoich.}} \tag{3.1}$$

where $\phi < 1$ signifies well ventilated conditions, whereas $\phi > 1$ denotes under-ventilated conditions. Since the over-all combustion process is studied in this work, ϕ is defined as

the equivalence ratio for the over-all combustion process. This is usually referred to as the *global equivalence ratio*, GER.

A phi meter was built and used for the measurement of ϕ [5]. The phi meter was originally constructed and calibrated for hydrocarbons [24], but some of the substances studied contain atoms of additional elements, namely nitrogen, sulfur and chlorine. Some exploratory experiments were therefore conducted, but no evidence has been found of influence that needs to be accounted for by the presence of these elements (see Sections 4.1 and 5.1).

3.2 Combustion experiments

The principal challenge as regards the large-scale combustions experiments was to achieve under-ventilated, *i.e.* oxygen-depleted, conditions. By varying degrees of restriction of the opening of the test chambers, the degree of ventilation was controlled.

3.2.1 ISO 9705 room set-up

Tests were performed inside a lightweight concrete room with dimensions in accordance with ISO 9705 [25] (see Figure 3.1). The room has one opening, 0.8×2.0 m^2, centrally located on one of the shorter walls. To alter the ventilation conditions inside the room, different heights of the opening were used: 0.89 m, 0.68 m, 0.56 m and 0.45 m, respectively. The width was kept the same in all tests. In this way, both well ventilated and under-ventilated conditions were managed. The soffit of the opening was kept at the same height (2.0 m above the floor in the room) for the whole series of tests and the sill was raised using non-combustible fibreboards.
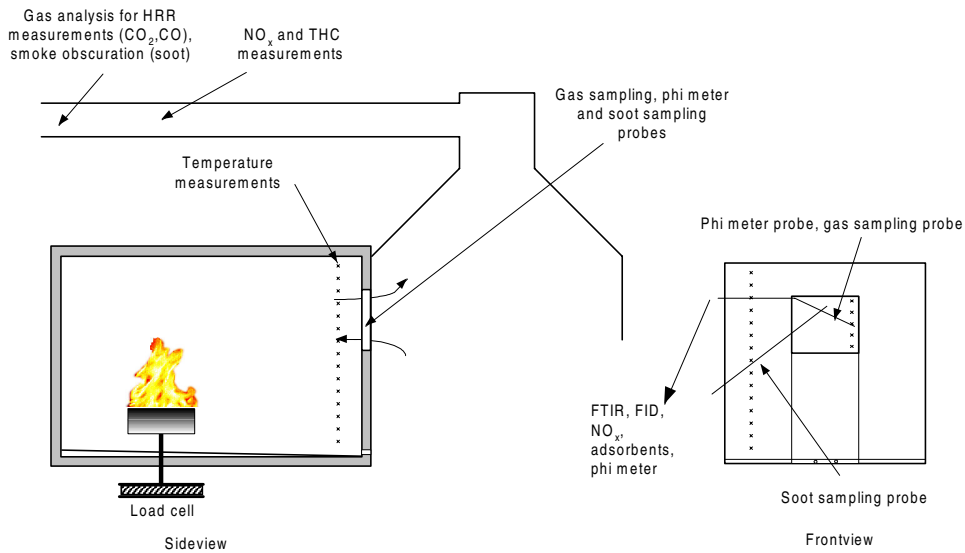
Figure 3.1   *The large-scale experiment set-up including the ISO 9705 room with the dimensions $3.6 \times 2.4 \times 2.4$ m^3 and the probe positions in the opening and in the exhaust duct to the calorimeter system.*

The fuel was put into pans of different size, 0.5 m^2 to 1.4 m^2, aimed at generating about the same total heat release rate, HRR, irrespective of substance. A load cell was used to measure the mass loss rate, MLR. To keep the fire plume away from the opening, the pan/load cell was placed on the centre line, equidistant from three of the walls, two thirds

of the length of the room from the opening. In some tests, a *sprinkler* was used to study the effect on the chemistry of the fire from the application of water. The water flow was chosen so as not to suppress or extinguish the fire, but rather to control it. For a listing of the ISO room experiments, see Table A1.1 in Appendix 1.

The only instrumentation inside the room was a thermocouple tree with 15 thermocouples in the front left corner (see Figure 3.1). The purpose of this thermocouple tree, besides just recording the temperatures, was for the temperatures to be used in calculations of the mass flow through the opening (see Section 3.3). The temperature profile from a smaller vertical thermocouple tree in the opening was used to define the areas of in- and outflow through the opening. These temperatures were also needed for converting the mass flow rate to a volume flow rate.

A hood connected to an exhaust duct [25] collected the combustion gases from the room. In the duct, the gas temperature and the flow rate were measured, and gas was sampled and transported to the gas analysis equipment. Concentrations of CO_2, CO, THC (total amount of unburned hydrocarbons) and NO_x (nitrogen oxides) were measured. A lamp/photo-cell system was used to measure the light obscuration, facilitating calculation of the soot production. HRR was determined using the production rates of CO_2, CO, soot and THC.

In the opening, gas samples were taken to the FTIR (Fourier Transform InfraRed spectrometer), the NO_x and the THC instruments, to the adsorption tubes, and to the phi meter (see Section 3.4). Sampling of soot particles was also performed in the opening.

3.2.2 Storage configuration set-up

The storage configuration tests were carried out in the larger test enclosure (see Figure 3.2) built beneath the industry calorimeter [26] in SP's fire hall. The dimensions of the enclosure were $8.9 \times 6.0 \times 4.8$ m^3, with an opening on one of the long sides. The size of the opening, 0.8×0.89 m^2, was the same as the largest opening used in the ISO 9705 room tests (see Section 3.2.1), with the soffit 1.5 m from the ceiling.

In these tests, the material was put in eight cardboard boxes, positioned on steel shelves in a two-tier post pallet system as shown in Figure 3.2. The substances were put in paper bags. Each bag contained 1.1 kg of substance. Eighteen bags were distributed on two levels in each cardboard box. The total amount of substance in the storage configuration tests was 160 kg, not including the cartons.
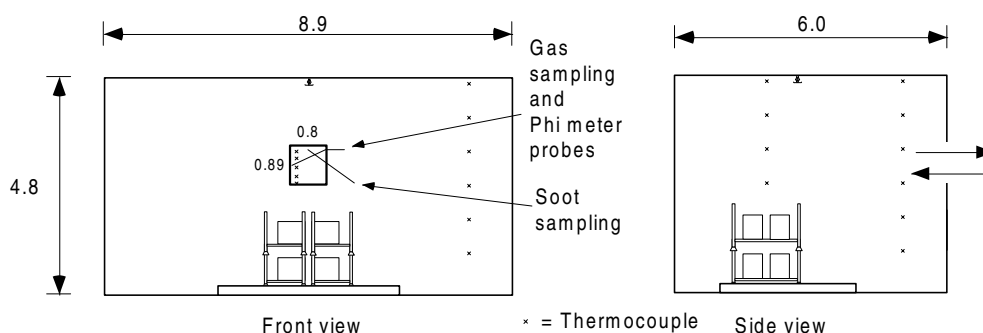

Figure 3.2 *The storage configuration set-up with the test enclosure, the thermocouples and the sampling probe positions in the opening; dimensions in are in meters.*

After screening tests, it was decided, for safety reasons, *not* to burn chlorobenzene as originally intended in bottles within boxes on shelves, but instead to put the fuel in an

open pan placed on a load cell. This set-up was also used in one of the two polypropene tests. This made it possible to compare in one case the effects the test enclosure itself had on the results. No load-cell was used in the pallet configuration tests. The mass loss was instead calculated, using the HRR and a combustion efficiency of 0.6 [2]. For a listing of the tests carried out in the storage configuration enclosure, see Table A2.2 in Appendix 2.

As in the ISO room tests, the only instrumentation inside the room were the thermocouples [5], two thermocouple trees and a set of thermocouples beneath the ceiling (see Figure 3.2). A smaller vertical thermocouple tree in the opening helped define the areas of in- and outflow through the opening.

The parameters measured and the sampling equipment used, in the duct and in the opening, were as in the ISO 9705 room tests (see Section 3.2.1), with the exception of the sampling probe for THC and NO_x in the duct which was the one described by Månsson et al. [27].

3.3   Sampling position and definition of flow

After-burning in the excess air was thought highly likely for the hot smoke gases escaping from the room, in particular for the under-ventilated fires. Further, substantial dilution of the smoke would occur as it was drawn through the duct (see Figures 3.1 and 3.2). Therefore, sampling in the duct for the measurements of ϕ and for the characterisations of the smoke gas components was considered less suitable and sampling in the opening was chosen as the preferred strategy.

Samples were taken diagonally across the upper half of the opening through two stainless steel probes, each having from 7 to 13 (3.0 mm) holes, with the suction end of the probes in the top corner; for a more detailed description, see the experimental reports [1, 2]. The probe for the phi-meter sampling had its holes inwards to include the soot with the sampled gas, whereas the other probe had the holes turned outwards to exclude the soot as far as possible.

Primarily, concentrations of the components are measured, but since they depend on various dilution factors they are not suitable in comparisons of results obtained under different conditions such as different scale. Yields, *i.e.* the amounts of individual components formed in relation to the amount of material combusted at some defined period of time, have a more invariant character. Yield is therefore the more relevant parameter for comparison of results.

To calculate, for example, yields for the reaction products, the mass flow is required for the smoke leaving through the opening where the sampling is performed. It is a difficult task to use velocity and temperature sensors in the plane of the opening to establish the mass flow rates. With scrupulous attention to detail, such techniques can be used for steady-state fires [28, 29], but for transient fires, the results are often nonsensical [30]. This originates from the following:

The outflows in the door opening have a velocity component in directions other than just the normal to the exit plane. With the commonly available velocity probes, this component is partially assigned − erroneously − to the normal direction.
For some fires the velocity distribution is not uniform across the width of the opening. Not only is the velocity different near the edges, but some fires also show [30] a stagnant region near the centre, and higher velocity flows away from the centre. The velocity measurements obtained are usually highly noisy, since the pressure difference is only a few pascals due to the low flow.

These considerations suggest that some means other than using direct measurement techniques should be used to assess the mass flows in the opening. There are different models available for calculating the flow. The model chosen has been described by Babrauskas [31] and assumes a well-stirred uniform-temperature compartment, signifying uniform density inside the compartment. The calculations are based on temperature measurements only and assume that the outflow and the inflow are equal. This model was refined to include the MLR [5].

3.4   Smoke gas characterisation

Detailed characterisation of the individual products of combustion was perhaps the most important SP task in the project. On-line, as well as periodic sampling and measurement techniques were used, *e.g.* FTIR [3] and adsorbents [4], respectively. An over-view of the main system for sampling of the smoke leaving the room is shown in Figure 3.3.
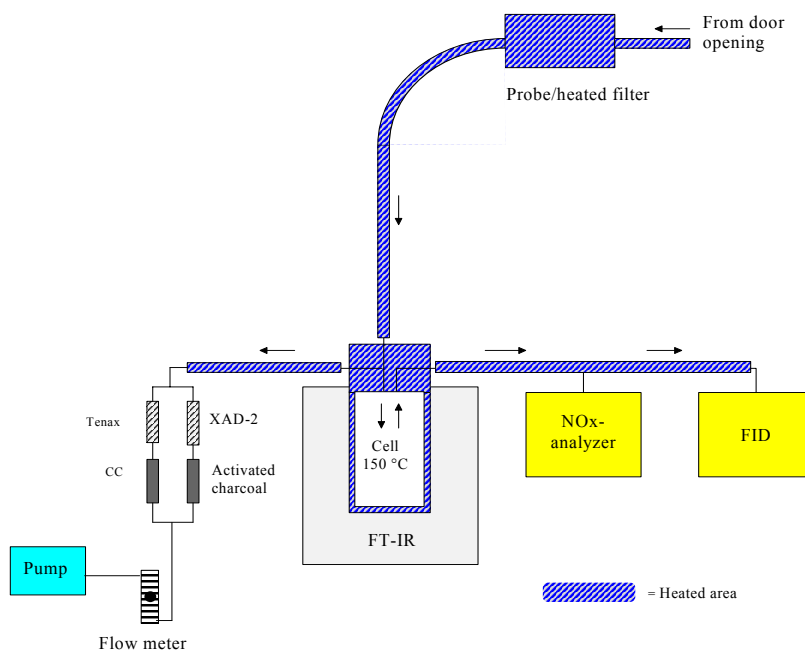
Figure 3.3   Sampling system for the characterisation of species in the smoke leaving through the test chamber opening.

The FTIR and the adsorbent techniques were utilised to measure quantitatively the concentrations of the individual components in the smoke. The parallel measurements of mass loss rate facilitated the evaluation of yields (see Section 3.3).

3.4.1   On-line measurements

One of the real advantages of continuous on-line measurements is that it allows evaluation of results over test periods that do not have to be selected beforehand.

The on-line instruments for measurements in the opening were, in addition to the phi meter, an FTIR spectrometer, a flame ionisation detector (FID for THC analyses) and a chemiluminescence instrument (NO_x). The dedicated NO_x analyser was used because of the superior resolution by the chemiluminescence technique, in spite of the possibility of utilising the FTIR also for the nitrogen oxides. The same types of instrument were used for measurements of NO_x and THC in the duct.

The obvious advantage of the FTIR measurement technique in fire testing, is the possibility to measure the concentration of a number of components in the fire gases simultaneously. Of primary interest was the production of CO_2, CO, HCN, HCl and SO_2. Other generally used methods for the last three of the species mentioned, *e.g.* absorption in a liquid, give a mean value of concentration for the particular sampling period. Generally, different methods of sampling and subsequent analysis would then have to be applied for each of the components.

Another valuable advantage of the FTIR technique is the possibility to obtain information in the spectra on additional species, such as *e.g.* the identification of carbonyl sulfide, COS, in the under-ventilated parts of the tests on the sulfur containing substance thiuram monosulfide.

A specific obstacle in FTIR measurements on fire effluents is the presence of water, one of the main components from the combustion of organic materials. This problem can, however, be handled by special measures taken in the evaluations and in the calibration of the instrument. A more detailed account of the FTIR measurements, including calibration and evaluation procedures, is given in a separate report [3].

3.4.2   Adsorbents

Two lines of adsorbents (see Figure 3.3) were used in the sampling of the smoke from the opening of the test chambers, each line made up of adsorbents for the highly and the less volatile organic components in the smoke, respectively. Carbotrap/Carbosieve (CC) – Tenax adsorbents were chosen because of the advantage of *thermal desorption* in the subsequent gas chromatographic quantitation/identification step. The principal advantage is that there are no solvent dilution or interference effects. A disadvantage is that the entire sample is spent in one analysis. For the activated charcoal–XAD-2 adsorbents, desorption is effected by a solvent. This may interfere in subsequent analysis by *e.g.* gas chromatography, GC, but allows repeated measurements, and the use of additional analysis techniques such as liquid chromatography, *e.g.* HPLC.

Benzene is expected to be more or less completely retained on Tenax for the sampling volumes used. The more volatile components in the smoke largely pass through the Tenax, but are retained on the CC adsorbent, or retained in varying proportions on both adsorbents. The CC adsorbent, in addition, is more suitable for polar compounds. Even though not shown in Figure 3.3, two parallel CC–Tenax adsorbent lines were utilised, the idea being to sample a smaller amount for identification of components by mass spectrometry (MS), and the other set with an approximately 5 times larger amount for quantification utilising a flame ionisation detector (FID).

The adsorbent sampling periods were ten minutes in most cases. The beginning of the sampling periods was chosen beforehand, or else initiated when a steady-state period appeared to be approaching. This meant that the selection of periods of sampling at specified degrees of ventilation was not as well controlled as intended.

The individual adsorbent tubes, primarily the CC and Tenax adsorbents, were analysed by GC. Quantitations were generally made utilising FID technique, identifications by mass spectrometry. A separate report describes the details on the sampling and analysis [4].

4 Evaluation of results

4.1 Heat release rates

The aim was to reach steady-state conditions during the major part of each test with an HRR of about 1000 kW. It was, however, only in one of the chlorobenzene tests (CB4) that a near steady-state period at about 1000 kW could be realised. In most of the tests, the steady-state HRR obtained was only about 500 kW and the level decreased as the opening height was decreased. In some tests, especially on polypropene, a second, higher steady-state period could be seen.

Because of an oxygen-instrument problem, all calculations of HRR values [5] are based on the *Carbon Dioxide Generation* strategy [32], rather than the more often used *Oxygen Consumption* method [33, 34].

4.2 Degree of ventilation – equivalence ratios

In the TOXFIRE ISO 9705 room tests, opening sizes were estimated and decided upon aiming at reaching steady state periods with equivalence ratios of 0.5, 1.0, 1.5 and 2.0 and with a HRR of about 1000 kW. At that point it was assumed that the total HRR would remain essentially constant independent of the size of the opening, while only at highly vitiated conditions the ratio between the amount of fuel burning inside the room and outside the opening would change. In fact, in these experiments the restricted ventilation affected the conditions inside the room in such a way that the total HRR was decreased and not only the part burning inside the room. However, the conditions inside the room were still under-ventilated. Only a few tests gave a long steady state period with constant ϕ and in those cases, the ϕ-value was rather low (*e.g.* Ny2, see Figure 4.1a). In many tests both HRR and the ϕ-value varied substantially within the same test.
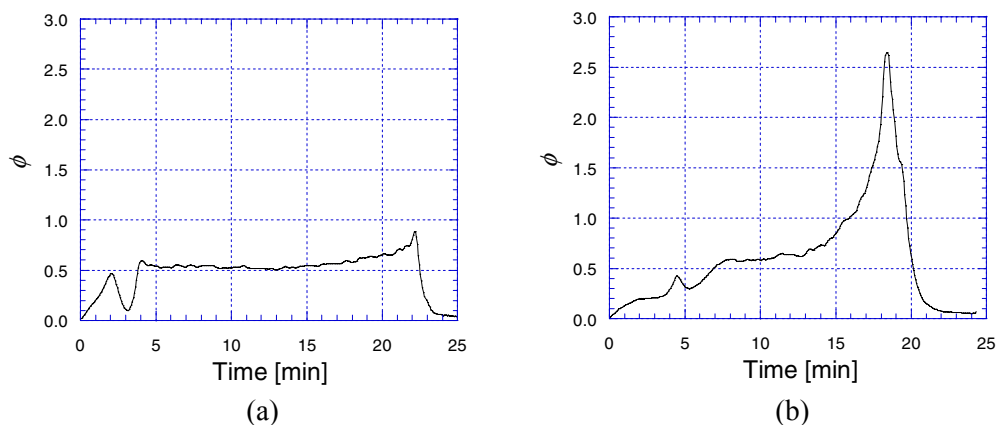
Figure 4.1   Global equivalence ratios for (a) Ny2 and (b) TMTM2.

Almost all the tests had a short steady-state period in the beginning with equivalence ratios between 0.5 and 0.8. The development after that varied considerably between the different substances. Some tests never reached ϕ values higher than 0.8, but those reaching equivalence ratios in excess of 1, all had a very fast increase through ϕ equal to 1.0. For $\phi > 1$ there were also clear differences. In tests with the thiuram monosulfide, the fast increase continued until the fire was manually extinguished (see Figure 4.1b), while in other tests (*e.g.* Ny4) ϕ reached a second plateau with an almost constant ϕ value between 1.0 and 1.5. The ϕ values for chlorobenzene are somewhat uncertain since they

were calculated from the MLR curve and in those tests considerable turbulence inside the room made the MLR signal very noisy.

Comparisons between values of the equivalence ratio measured with the phi meter and values calculated from the mass loss rate of fuel and the mass flow of air do not show any systematic differences that can be attributed to the presence of heteroatoms in the molecules of the test substance [5].

For the storage configuration tests, no attempt was really made at designing the experiments such that a pre-determined variation of the degree of ventilation would be achieved.

4.3   Yields from on-line measurements

For the evaluation of yields at different equivalence ratios for each of the chemicals studied, it was necessary to select short time periods with reasonably constant ϕ values within a test and calculate yields for these periods. It would have been preferable with longer periods of averaging to minimise the influence of noise. An advantage was, however, that several values of the equivalence ratio could be used from the same test, which increased the total number of useful data points.

The strategic choice to use, as far as possible, on-line measurement methods turned out to be a sound one, since this allowed assessing the concentrations of the individual components for precisely the time slots chosen of the *constant ϕ* values. It also allowed comparisons of results for comparable ϕ values obtained from different combustions of a particular material.

4.4   Adsorbents

The results of the adsorbent measurements were, of course, the integrated mean values over the sampling period, pre-selected for the individual combustion experiments and hence it was not possible to select the range of ϕ values afterwards. The range of ϕ values was thus more limited for the adsorbent results than those for the other parameters.

Nearly all results were derived from GC analysis of the larger amount Tenax and CC adsorbent tubes (see Section 3.4.2), adjusting the split to suit the amount sampled, determined on an ether extract of the corresponding XAD-2 adsorbents [4]. Yields were calculated from the amount of the individual components determined using the FID, volume of gas sampled, total flow through the opening (calculated; [5]) for the sampling period and the corresponding mass loss of the material burned. Identifications were based on the simultaneously performed MSD measurements.

The presence of methane in the smoke gases from many of the tests was verified by FTIR. This was valuable information used in the interpretation of the results from analysis of organic species in the smoke [4].

5 Discussion of the results

Detailed results from the individual combustion experiments are given in the individual experimental reports [1, 2], in terms of table listings and in graphs as functions of running time for the tests. In addition, graphs are shown of yields in the opening of the ISO room as functions of ϕ and temperature, respectively, for the individual materials studied [1]. For polypropene, Nylon and the thiuram monosulfide, the results are comprehensive ones. The chloronitrobenzoic acid did not burn at a reasonable rate by itself in the ISO room, but had to be boosted by polypropene making the interpretation of the results less straightforward. The large proportion of soot from combustion of chlorobenzene clogged the sampling lines. As a result, the sampling was deficient in some of the chlorobenzene tests. A listing of all of the individual tests performed is given in Appendix 1.

5.1 Combustion reaction and equivalence ratio

For the proper interpretation of ϕ, it is necessary to define the stoichiometric reaction. For hydrocarbons, this is simply the reaction where carbon is quantitatively oxidised to CO_2 and all hydrogen forms H_2O, which for fires is water in the gaseous phase.

With nitrogen in the compound, a fraction of it yields NO_x, the amount being dependent on the combustion temperature and the type of nitrogen bonding in the substance in addition to the availability of oxygen. Only a minor fraction of the large excess of nitrogen accompanying the air oxygen yields NO_x, again depending on combustion temperature and the availability of oxygen. Most of the fuel nitrogen does, however, end up as N_2 gas in the smoke. Therefore, the stoichiometric reaction for nitrogen-containing organics is defined as having nitrogen quantitatively as N_2 in the combustion products.

For sulfur-containing organics, the sulfur in combustion at atmospheric pressure in air yields SO_2 and this is taken as the stoichiometry-defining combustion product. For comparison, combustion in pure oxygen at 3 MPa in a calorimetric bomb predominately has SO_3 as the sulfur-containing combustion product, which then quantitatively yields sulfuric acid with the water formed. SO_2 would be a poor choice in the latter case.

Combustion of organo-halogen organics in high-pressure oxygen in a calorimetric bomb yields a mixture of free halogen and hydrogen halide. For organo-chlorine compounds about 4 % of the halogen yields free chlorine, Cl_2, and the remainder HCl. For organo-bromine substances the ratio is reversed, $i.e.$ about 96 % is free bromine, Br_2, and only 4 % HBr is formed initially in the combustion. In fires, Cl_2 has not been detected in the smoke at levels of the order of a few tenths of a per cent. Either none is formed in the combustion, or limited amounts of Cl_2 react immediately with incompletely oxidised intermediates in the hot combustion gases. For the stoichiometric reaction, the reaction product for chlorine is defined as HCl. For bromine-containing compounds, free bromine is reported to have been found in significant amount in the smoke [35].

When phi-meter measurements are applied to define the equivalence ratio, $i.e.$ the degree of ventilation, it is necessary that the compounds exiting from the phi meter are consistent with the reference compounds selected for the stoichiometric reaction. It has been verified, for example, that the combustor did not convert any HCl into Cl_2 (g).

It is worth pointing out that even when enough oxygen is present for complete oxidation of $e.g.$ carbon to CO_2, significant amounts of CO are formed. The amount depends on the equilibrium constants for the reactions at the temperature where the reaction freezes, $i.e.$ the temperature where the reaction rate has decreased to a level where further reactions have ceased to occur.

Carbon monoxide formation is complex and difficult to predict using simple models. One complicating side reaction is the disproportionation reaction of carbon monoxide to yield gaseous carbon dioxide and solid carbon, *i.e.* soot.

$$2\,CO\,(g) \;\rightarrow\; CO_2\,(g) \;+\; C\,(s) \tag{5.1}$$

5.2   Sampling position

In Section 3.3 a description of the sampling position can be found. There is also a short discussion about why this position was chosen. In this section some problems arising from the choice of sampling position are discussed.

One of the challenges in the large-scale tests was to perform reliable FTIR measurements on the, more or less, undiluted smoke gases in the opening of the test enclosure. The choice of this sampling position resulted, generally, in measurements on high concentrations of the main species, including interfering species such as water. Comparison of our results with those from the other project partners (VTT and Risø), in terms of the concentration levels of gases measured by FTIR, shows that generally the concentration levels in our tests are higher, but less than an order of magnitude.

There are suspicions that faulty sampling might have occurred at the lowest mass flows through the opening, caused by suction of small amounts of outside air into the sampling probe. The flow regions in the opening should, however, very quickly be established and during a large part of the each experiment the outflow region covers more than half of the opening. During this time period the outflow was also often very intense minimising the risk for sucking fresh air. Also, the entrainment of fresh air into the flow of combustion gases taking place in the window opening should not influence the gas sampling. The entrainment of air inside the room of course affect the sampled gas concentrations, but this extra air is a part of the total flow and should not be designated an error. There is however a short period of time where the flow around the sampling probes is unstable and that is when the equivalence ratio passes one. The flames then come out through the opening and it was burning around the probes. In some tests the flow was also pulsating increasing the uncertainties. When the conditions turned even more under-ventilated it was burning outside the room and the flow was again stable.

The measuring in the duct is more straightforward. The flow is more stable and more well defined making the determination of the flow easier. It would have meant more optimal concentrations for some of the FTIR measurements and since the concentration of soot is much less there is no problem with clogging of the sampling probes. For the adsorbents, however, longer sampling periods might then have been required.

Considering the circumstances discussed above, a conclusion that lies near at hand is that one should sample the gases in the duct and not in the opening. That would make the evaluation much easier, but since there are differences between the two positions the decision must be based on what phenomenon that are of interest to study. In a flashover situation with flames outside the room, the unburned gases are combusted outside the room. The situation differ very much between the opening and the duct and if one wants to know what is leaving the room and is interested in how the results are connected to the global equivalence ratio of the room, the sampling position ought to be in the opening. If it instead is of interest to know what the final products are a distance away from the fire, it would be recommended to perform the sampling in the duct.

For the storage configuration measurements, the dilution factor for the smoke in the duct would be larger than for the ISO room tests. The time for the gases from the fire to reach the opening is also different in the two experimental cases. Further, the drop in temperature of the already rather cool smoke exiting through the opening would not be advantageous in the storage configuration experiments. Hence, sampling in the opening would in this latter case be the preferred arrangement.

5.3   Comparison between ISO room and storage configuration tests

A comparison of the results from the ISO room with those from the storage configuration tests should give valuable indications as to whether the magnitude of the ISO room tests were sufficient to represent real fires. Did the ISO room yield combustion products of the same types and in about the same amounts as do real-scale fires? General trends regarding yields of important combustion products are discussed in the following.

To get an understanding of the physical conditions of the two scales, the HRR and the temperatures in the two test enclosures are compared. In the storage configuration tests, comparable behaviour of the fires was observed for all the materials tested. The HRR increased quickly to a steady-state close to 1000 kW; see Figure 5.1 The fast rise of the fire was probably an effect of the configuration of the materials and of the easily ignited cardboard boxes. The fire behaviour in the ISO-room was more variable and differed between different materials. Often, two stages could be observed in the fire. First the fire reached a comparatively low level of HRR determined by the ventilation conditions. As the radiation from the walls increased and flash-over occurred, the fire extended out through the opening and a steep rise in the HRR was seen; see Figure 5.1.
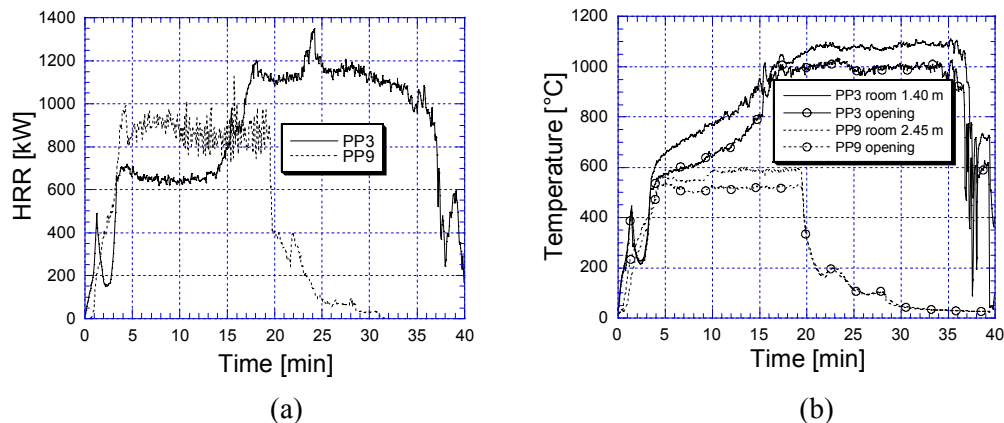

(a)   (b)

Figure 5.1   Development of HRR (a) and temperature (b) for one ISO room test (PP3) and one storage configuration test (PP9).

The influence of the larger volume of the combustion room is most obvious as regards the temperatures inside the room. In the storage configuration enclosure, they were lower than in the ISO-room, often by 200 K or more. The fire load in the configuration tests was insufficient to yield very high temperatures. In the two-tier configuration tests the temperature as recorded in the corner of the room was only about 600 °C. This implies problems with condensation of *e.g.* hydrochloric acid on the walls. Further, the larger volume brings about non-uniform gas composition in the room, and a slower response in the measurements of the gases produced in the actual combustion. In comparison with the

ISO 9705 room tests, the combustion behaviour of the substances developed more slowly. In several cases a period of steady-state conditions was established. The combustions were formally well ventilated (ϕ<1) in all cases, as measured by the global equivalence ratio.

In many cases, a clear correlation was found between the two configurations regarding the yields of the combustion products and their dependence on the degree of ventilation.

Nylon 66 is an example of a material, which showed a correlated behaviour for all the combustion products measured. As an example, yields of HCN and CO versus the degree of ventilation for Nylon are shown in Figure 5.2.
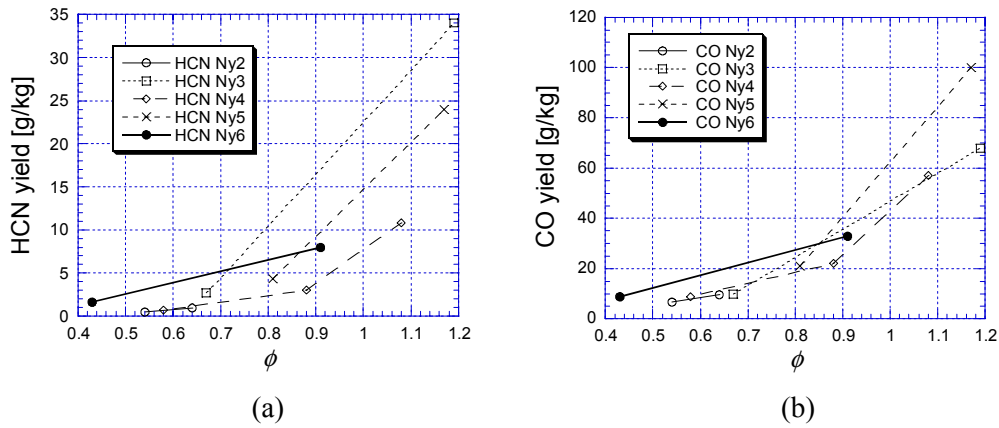

Figure 5.2   Yields of HCN (a) and CO (b), respectively, for Nylon 66 from four different ISO room tests and one storage configuration test (Ny6).

The consistency in the correlation between the two configurations for the tests on Nylon 66 indicates that the assessment of the mass-loss in the storage configuration test, in short described in Section 3.2.2, was valid [2]. It also implies that the measurements of the degree of ventilation were analogous in both of the configurations. Graphs of the concentrations as functions of ϕ of the on-line components normalised against CO_2 concentrations was prepared to make up for lack of measured mass loss in the storage configuration tests. These graphs produce about the same over-all pictures as the yield graphs and they are not included here.
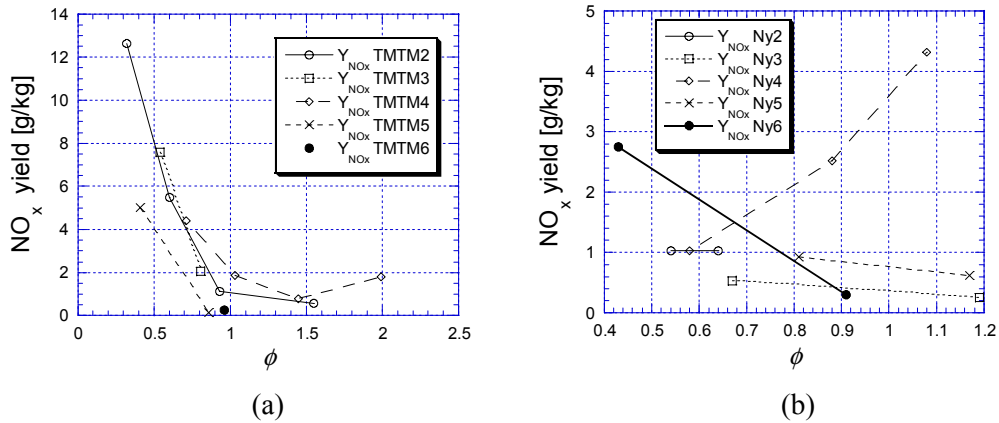

Figure 5.3   Yields of NO_x for thiuram monosulfide (a) and Nylon 66 (b) from four different ISO room tests and one storage configuration test (Ny6 and TMTM6 are storage configuration tests). Observe the different scales on the axes.

One particularly interesting observation regarding the production of NO_x was made in the Nylon tests. The results from the storage configuration test correlated well with those from the ISO room and with what would be expected from the dependence on the degree of ventilation. In one of the ISO-room tests, however, irregular behaviour of the NOx production was observed. This is probably an effect of temperature, as in this test significantly higher temperatures were attained. The production of NO_x for Nylon as a function of the degree of ventilation is shown in Figure 5.3.

For some tests in the storage configuration, an unexpected phenomenon regarding the degree of ventilation was noticed. For all the products of combustion in the tests on thiuram monosulfide and polypropene, there is a displacement of the yield-values as compared to the results from the tests in the ISO room. The deviation is in the more well ventilated direction (lower ϕ value). In Figure 5.4 this effect can be seen for HCN and THC in the tests on thiuram monosulfide. Even though oxygen is present in excess inside the large volume of the room, oxygen may not have been available to the fire as such, perhaps from lack of sufficient turbulence for effective mixing of the gases or too rapid a drop in temperature. The indications of locally under-ventilated conditions are supported by the formation of significant amounts of COS together with seemingly high CO yields. COS was observed for thiuram monosulfide in the ISO room for under-ventilated conditions only. Adsorbent results for polypropene support the hypothesis of local under-ventilation.
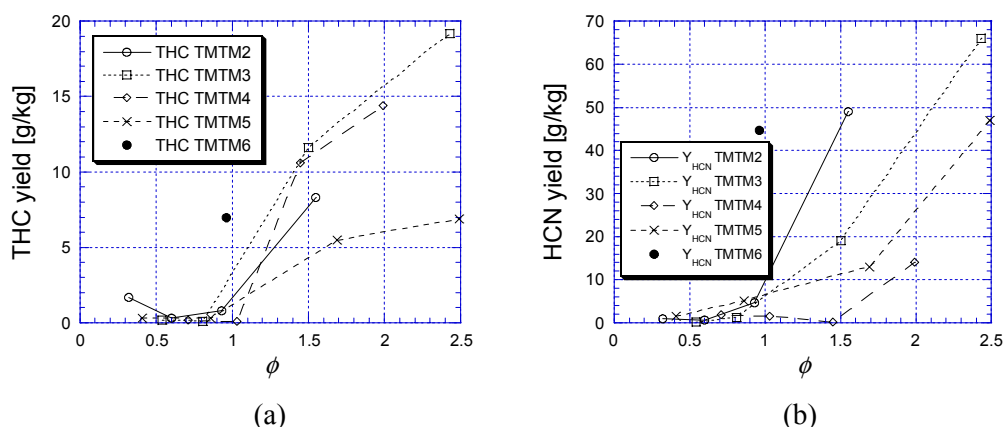

Figure 5.4   Comparison of yields of THC (a) and HCN (b) from the thiuram monosulfide ISO-room tests and the storage-configuration test (TMTM6).

The main individual organic components found in the smoke gases from the substances tested in the two experimental configurations are listed in Table 5.1. This table contains only summarized qualitative information for comparison; however, all the main components were quantified in the two test series [1, 2].

In the ISO 9705 room experiments, several tests were performed with each substance. Thus, in Table 5.1 only the overall production patterns regarding the main species found in these tests are shown. For the storage configuration tests, the identified main species are listed in order of magnitude.

The general production pattern of the species found from the large-scale tests on PP and Ny agrees well with what has been reported in the literature on pyrolysis/combustion work in the small scale [36, 37]. In the case of PP, mainly aromatic species as benzene, toluene and naphthalene were found. This is in fact an obvious characteristic of all materials tested. Irrespective of whether the material combusted is aliphatic or aromatic in

its chemical structure, benzene is one of the principal components and is often one of the species with the highest yields among the organic smoke gas components. In the tests on Ny, nitrogen-containing species as benzonitrile and 2-propene nitrile were found, in addition to aromatic hydrocarbon compounds.

Table 5.1   Main individual organic species found in the combustion experiments.

Substance	Principal organic species ISO room tests	Principal organic species Storage configuration tests
PP	Benzene Naphthalene Toluene Propene Ethynylbenzene Styrene	Benzene Propene Naphthalene Toluene Propyne Styrene
Ny	Benzene Naphthalene Benzonitrile Ethene 2-Propene nitrile Ethynylbenzene Toluene Acetonitrile	Propane Benzene Toluene Cyclopentanone Benzonitrile 2-Propene nitrile
TMTM	Acetonitrile Benzene Acetic acid Propene CS_2 Isothiocyano methane 2-Propene nitrile Bensoenitril Thiophene	Propene Acetonitrile Benzonitrile Benzene 2-Propene nitrile Thiophene CS_2
CNBA	Chlorobenzene Dichlorobenzene Chlorobenzene nitriles Benzene Benzonitrile Naphtalene	Chlorobenzene Dichlorobenzene Propene Chlorobenzene nitriles Benzene Benzonitrile
CB	Chlorobenzene Benzene Naphthalene Ethynylbenzene Biphenyl	Chlorobenzene Benzene Naphthalene Chloroethynylbenzene Ethynylbenzene

TMTM contains both nitrogen and sulphur in the chemical structure. In these tests, several nitrile compounds were found as well as sulphur containing compounds as thiophene and CS_2. A more detailed account for the organic species produced in the tests with TMTM can be found in Table 5.2, where yields of the individual compounds found in the ISO 9705 room tests are presented.

Two of the substances tested, CNBA and CB, contained chlorine. Chlorobenzene was the major organic compound found for both of these substances and this is more or less what could be expected. In the case of CB, the chlorobenzene found probably is the survival

fraction of the original substance. CNBA contains one chlorine atom bound to a benzene group in the chemical structure, which explains the production of chlorobenzene. Other major compounds found in the tests with CNBA were nitrile-compounds, as in the tests with the other nitrogen-containing substance, Ny.

One drawback with the results on organic species from the ISO 9705 room experiments, where under-ventilated conditions were attained, is that the sampling period for the adsorbents coincided with a ventilation degree higher than one only for experiments with TMTM and CB. The results presented for PP, Ny and CNBA, consequently, all refers to well ventilated conditions. In the four tests with TMTM in the ISO 9705 room tests, however, sampling of organic species was made during time periods giving a reasonable spread in the equivalence ratios for the periods. In Table 5.2, yields of the main individual compounds are shown for these tests. It should be noted that the ϕ-values stated in the header represent the average during the sampling period. For some of the species found, a clear dependence on the equivalence ratio can be seen, *e.g.* for acetonitrile and acetic acid.

Table 5.2   *Yields in g/kg for the main individual organic components found in the ISO 9705 room tests on TMTM.*

Compound	Averaged ϕ-value			
	0.84	0.96	1.06	1.33
Acetonitrile	0.14	0.25	0.72	5.51
Acetic acid	Minor	0.081	0.27	0.54
Benzene	0.12	0.073	0.058	Minor
Benzonitrile	0.060	0.049	Minor	0.090
CS_2	0.25	0.004	Minor	Minor
Isothiocyano methane	Minor	Minor	0.84	0.31
Propene	0.49	Minor	Minor	0.27
2-Propene nitrile	0.025	0.11	0.13	0.11
Thiophene	0.091	0.11	0.097	0.11

5.4   Comparison of results with those from other partners

For detailed comparisons of results from different scales the reader is referred to the work by Andersson et al. [12]. However, a limited comparison relevant for the SP results is given below. The tests most similar to those at SP are the LU medium scale experiments [10]. Unfortunately, $\phi > 1$ was attained in only one of their experiments. In the small-scale experiments performed at VTT, on the other hand, the equivalence ratio was sometimes higher than one [9].

No comparisons with the micro scale (Risø) have been performed since the less well-ventilated *fires* were, in fact, *pyrolysis* reactions [7, 8]. The expected presence of COS as disclosed by FTIR, however, was corroborated in the small-scale tests [8].

A comparison between the results from SP, LU and VTT has been made for the substances Nylon and TMTM. The yields found in the medium scale tests [10] were on the whole higher than the corresponding yields in both the large scale and the cone calorimeter scale. In the medium scale, almost no under-ventilated conditions were achieved, nor are there any ϕ-values for Nylon between 0.2 and 0.7. Still one can study the trends when ϕ approaches one. These trends look reasonable for most of the products. However, the NO_x yields for TMTM as a function of ϕ has an unexpected v-shape (see Figure 5.5) with an increasing value as the equivalence ratio approaches one.
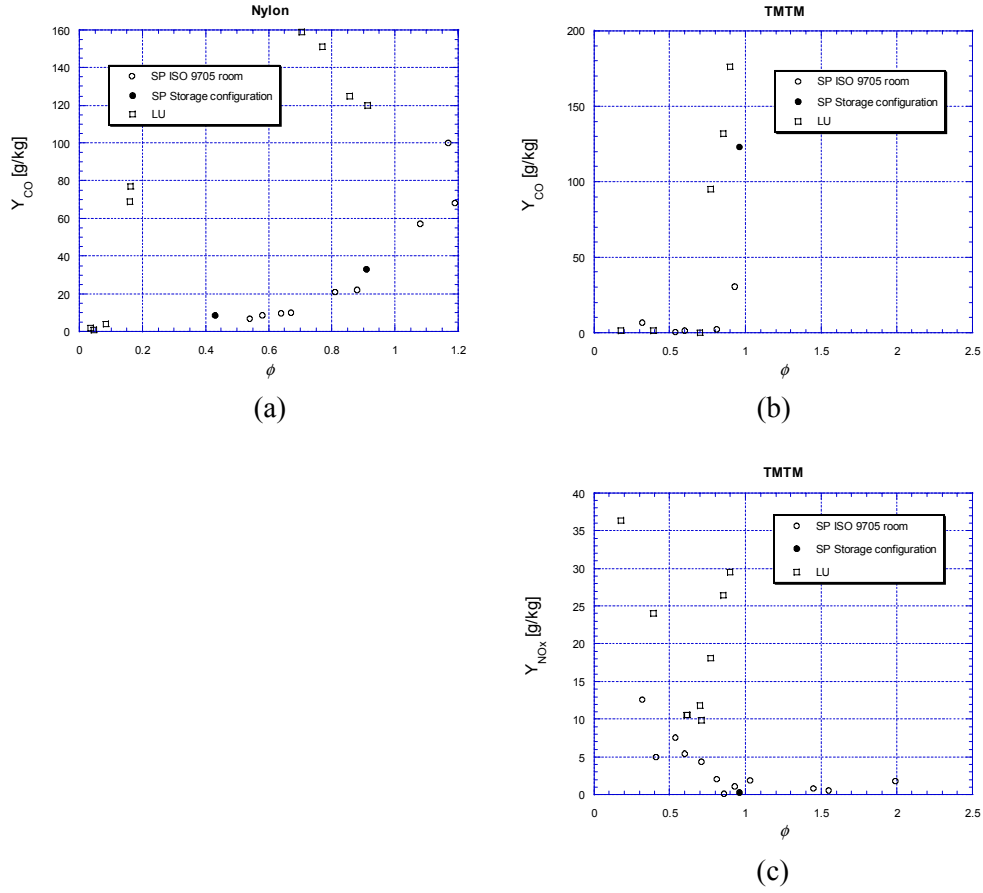
Figure 5.5   Comparison of yields of CO (for Nylon and TMTM) and NO$_x$ (for TMTM) from the large-scale tests (SP) and the medium scale tests (LU).
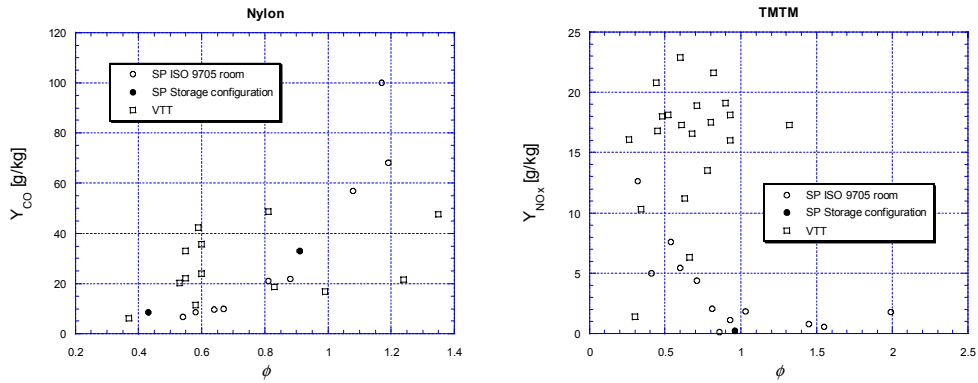

Figure 5.6   Comparison of yields of CO (Nylon) and NO$_x$ (TMTM) from the large-scale tests (SP) and the small-scale tests (VTT).

In the cone calorimeter scale [9], the yield values are very much scattered and no obvious function of ϕ can be observed (Figure 5.6). It should be noted that in the large scale tests and the medium scale tests the equivalence ratio was measured with a phi meter. In the cone calorimeter tests, on the other hand, the equivalence ratio was calculated and several different equivalence ratios were defined and used depending on the circumstances during

a test. The equivalence ratio used in the comparison mentioned here is the one called effective equivalence ratio related to the input of oxygen.

5.5 Comparison with results from other projects

Well-ventilated pool fires were studied in a previous project [38]. The combustion experiments were then carried out in open pools directly beneath the large hood of the SP industry calorimeter. Polypropene, Nylon 66 and chlorobenzene were studied in both projects. The amount of substances burnt in the previous project varied between tests, but was normally between 50 kg and 100 kg. This is equal to what was used in the ISO-room experiments. The results from the previous project showed good repeatability between tests, and the production pattern was considered to be likely for a well-ventilated fire. An interesting comparison should be that between the well-ventilated pool fires and the results from the tests in the ISO-room and the storage configuration, where the degree of ventilation varied and was measured.

CO and THC are interesting parameters for all substances tested, and the agreement between the test series was generally found to be good. The agreement is visualised in Figure 5.7 for polypropene and in Figure 5.8 for Nylon 66. However, the apparent displacement of the yield values for the tests performed in the larger test enclosure on polypropene are clearly shown from this figure; an explanation to this phenomenon was discussed in Section 5.2. In the well-ventilated pool fires, the degree of ventilation is unknown but is considered to be high (low value of ϕ). The average yield results from these tests are marked with a dashed line in the plots below, and it can be seen that these yields correspond with a high degree of ventilation in all cases. Also for chlorobenzene the agreement between the results from the two projects is significant, but the results are not as conclusive as there were fewer data points from the ISO-room tests for this substance.
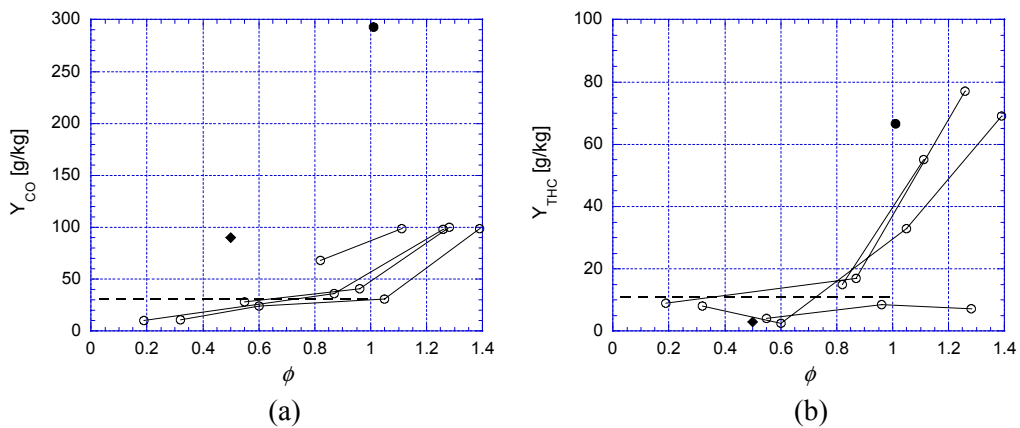

(a) (b)

Figure 5.7   *Comparison of yields versus ϕ for polypropene, a) CO yields and b) THC yields. (ISO 9705 room tests: -o-; storage configuration test in the LTE: ●; pool fire test in the LTE: ♦; open pool fire tests: ---)*
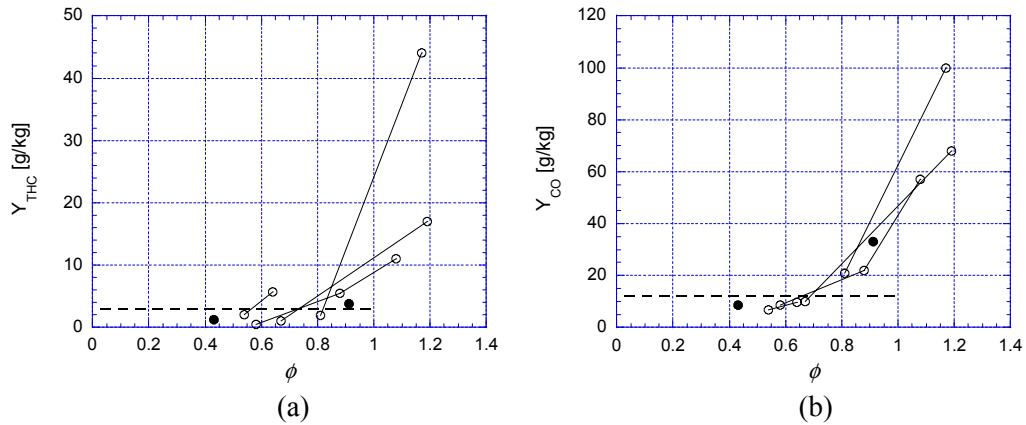
*Figure 5.8   Comparison of yields versus φ for Nylon 66, a) CO yields and b) THC yields.
(ISO 9705 room tests: -o-; storage configuration test in the LTE: ●; open pool fire
tests: ---)*

In the case of Nylon 66 also NO_X, HCN and NH_3 are interesting parameters measured in
both projects. For NO_X on-line chemiluminescence measurement technique was used in
both project, but in the earlier project, HCN and NH_3 was measured by drawing gas
samples through impinger bottles for subsequent analysis, giving results only as an
average over the sampling period. The good agreement found between the results for both
HCN and NH_3, which is visualised in Figure 5.9, indicates that the measurements were
made in a proper way, and valid production levels during well-ventilated large-scale fires
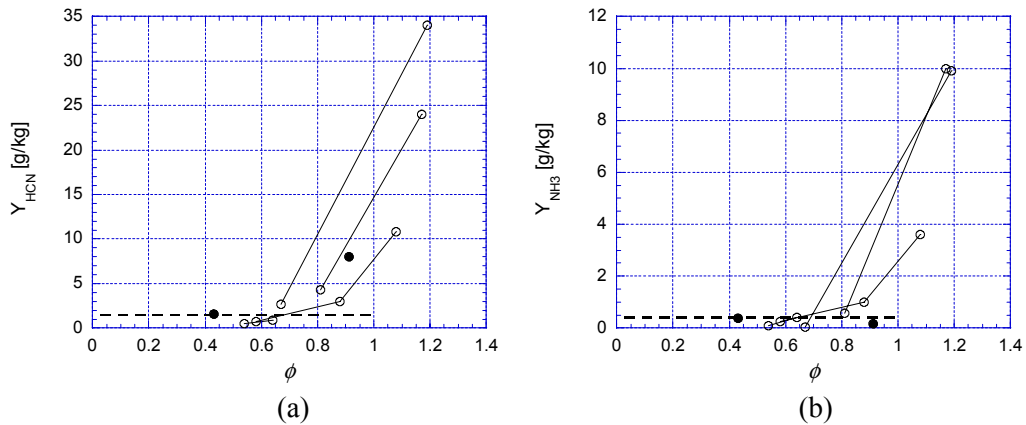are established.

*Figure 5.9   Comparison of yields versus φ for Nylon 66, a) HCN yields and b) NH_3 yields.
(ISO 9705 room tests: -o-; storage configuration test in the LTE: ●; open pool fire
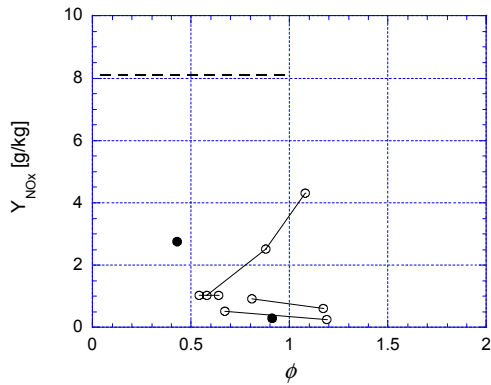tests: ---)*

Figure 5.10   Comparison of NO$_X$ yields versus ϕ for Nylon 66. (ISO 9705 room tests: -o-; storage configuration test in the LTE: ●; open pool fire tests: ---)

The correlation of NO$_X$ (Figure 5.10) was not as good as for other species produced, but the trend of higher yields at well-ventilated conditions was seen also in the earlier open pool fire experiments.

The only chlorine containing substance tested at SP both in the TOXFIRE project and in the previous well-ventilated open pool fire experiments was chlorobenzene. In the previous tests the yields of HCl was high, close to the theoretical maximum. In the TOXFIRE tests, on the other hand, the yields of HCl was lower, approximately half of the theoretical maximum. A possible explanation could be losses of HCl on walls in the enclosure, thus reducing the yield measured.

A more detailed comparison of the results from the different experimental series can be found in the work by Blomqvist [39].

6   Summary and conclusions

Generally, the large-scale tests have worked according to plan and yielded a multitude of valid, interesting results, in spite of the restraint that all the tests had to be performed in just one continuous period, without time for even brief intermediate evaluations of the results.

It has been shown that it is possible to attain under-ventilated conditions on a scale as large as that in the ISO 9705 room. Further, larger-scale fires such as those in the storage configuration facility do not appear to alter the outcome of the combustions significantly. The ISO 9705 room scale can hence be taken as a model for real-scale fires, at least as long as modestly complex systems in space are studied.

It has been demonstrated that, depending on the circumstances, the absence of long periods of steady state is no handicap. Instead, the possibility to select limited periods of time for evaluation of yields, HRR etc turned out to be greatly advantageous.

Sampling in the duct would simplify the sampling procedure as well as the evaluation of the results considerably compared to sampling in the opening. In particular, definition of the mass flow would be more straightforward. More of permanent installations would allow expeditious assembling of the instrumentation required for this type of rather extensive measurements. This would then allow even this type of effort to be spread over time with consideration of the results obtained from one set of experiments before performing the next series.

The use of on-line FTIR measurements in the large-scale tests has resulted in interesting and valuable information on the combustion gases produced. The methodology used, proved to fulfil the quantitative needs in this work.
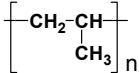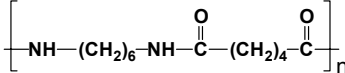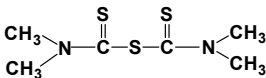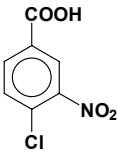
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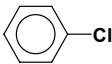
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Appendix 1 Fuel substances for the combustion experiments

Table A1.1   Substances selected for the large-scale combustion experiments [1].

Polypropene PP – $[C_3H_6]_n$	
Nylon 6 6 Ny – $[C_{12}H_{22}N_2O_2]_n$	
Tetrametylthiuram monosulfide TMTM – $C_6H_{12}N_2S_3$	
4-Chloro-3-nitrobenzoic acid CNBA – $C_7H_4NO_4Cl$	
Chlorobenzene CB – C_6H_5Cl	

Appendix 2 Identification of the SP TOXFIRE experiments

Table A2.1   ISO 9705 room combustion experiments [1].

Fuel Test Id	Opening height/m	Pool size/m^2	Fuel mass/kg
Polypropene			
PP3	0.89	1.2	60
PP5	0.68	1.2	60
PP4	0.56	1.2	60
PP6	0.45	1.2	60
Nylon 66			
Ny2	0.89	1.4	75
Ny4	0.68	1.4	75
Ny3	0.56	1.4	75
Ny5	0.45	1.4	75
Thiuram monosulfide			
TMTM2	0.89	1.2	60
TMTM4	0.68	1.2	60
TMTM3	0.56	1.2	60.5
TMTM5	0.45	1.2	60.5
Chloronitrobenzoic acid [a]			
CNBA1	0.89	1.4	74.5
CNBA2	0.89	1.4	60
CNBA3	0.89	1.4	40
CNBA4	0.45	1.4	60
Chlorobenzene			
CB3	0.89	0.5	45
CB4	0.89	0.8	51
CB6	0.68	0.8	50
CB5	0.45	0.8	50.5

Table A2.2   Storage configuration room tests [2].

Test Id	Opening height/m	Configuration	Fuel mass/kg
PP8	0.89	Pool 1.2 m^2	42.5
PP9	0.89	Bags in boxes	160
Ny6	0.89	Bags in boxes	160
TMTMT6	0.89	Bags in boxes	160
CNBA5	0.89	Bags in boxes	160
CB7	0.89	Pool 0.8 m^2	39.5