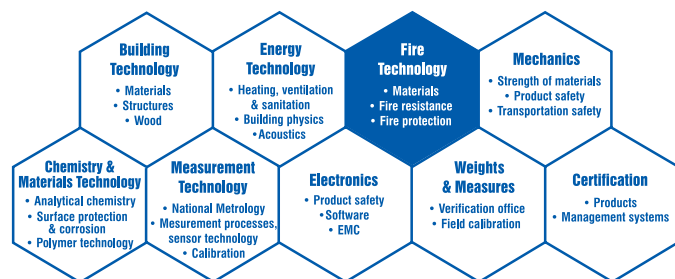


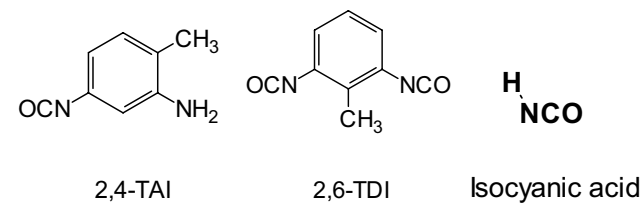
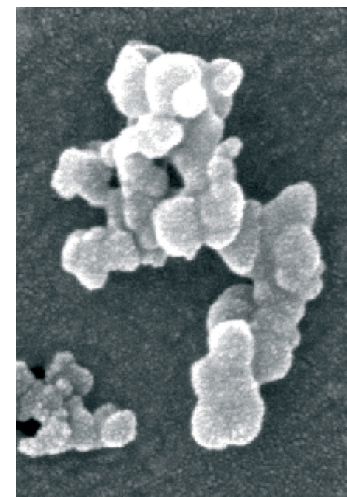
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Particles and isocyanates from fires

Brandforsk project 324-021



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SP Fire Technology
SP REPORT 2003:05

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Particles and isocyanates from fires

Brandforsk project 324-021

Abstract

The capacity for generation of particles and/or isocyanates as a result of combustion is presented in this report for 24 different building materials or products. Other gaseous compounds (e.g. HCl, HCN, SO₂, etc.) were also measured in the produced smoke. In addition to the standard building materials, a carbon fibre based composite material was tested in order to investigate if particles resembling asbestos could be generated.

The majority of the experiments were performed at small-scale in the Cone calorimeter (ISO 5660) but some data were also collected at an intermediate scale (SBI method, EN13823)), at full scale (Room-Corner, ISO 9705) or in other larger scale experiment. In the latter, personnel involved in the experiments were tested for isocyanate metabolites in order to estimate exposure hazards.

The amount and particle size distribution of the particles was measured by the use of a low pressure impactor that could differentiate between particles with an aerodynamic diameter from ~30 nanometer up to 10 micrometer. The isocyanates were collected both from the gas phase and from part of the respirable particle phase by means of an impinger bottle and a filter. Subsequently the isocyanate was quantified using LC-MS technology. Other gaseous compounds were measured using an FTIR instrument.

The results from the project show that the yield of particles generated varies significantly for different materials but that the shape of mass and number size distributions are very similar for all the materials tested. The maximum amount of particles was obtained from building materials that did not burn well (e.g. flame retarded materials). Materials that burn well, e.g. wood materials, tend to oxidise all available combustibles and thereby, minimises the amount of particles in the smoke gas.

The results for isocyanates indicate that it is possible to find fire scenarios where the greatest danger from the gases produced in the fire is actually related to their isocyanates content. The results also show that the isocyanate content should be included when estimating the overall hazard from fire smoke.

As the data produced is unique in this area and covers a restricted set of building products, more data should be produced before final conclusions can be drawn.

Key words: Particles, fire, isocyanate, composite, carbon fibre

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Preface

This project has been financed by the support of the Swedish Fire Research Board (BRANDFORSK, Project nr 324-021).

The reference group contributed with discussions and suggestions for improvements, and their assistance is gratefully acknowledged. The reference group consisted of the following people:

| | |
|-------------------|--|
| Cecilia Alfredson | The Swedish Rescue Services Agency |
| Mehri Sanati | Växjö University |
| Magnus Persson | Borealis AB |
| Curt-Åke Boström | IVL Swedish Environmental Research Institute |
| Lennart Nilsson | Perstorp AB |

Summary

There has been an increasing awareness of the health and environmental impact from particles generated in combustion. In spite of this and in spite of the health hazards related to large quantities of particles generated in a building fire, few reports have been made on this particular combustion process. In this report we show the mass- and number density distribution of particles generated from combustion of different materials and products. We also show the total particle yields. One particular material tested was a carbon fibre composite. Such material has been suspected to have the capability of generating asbestos-like particles in a fire situation. We found that this could happen in a vitiated fire scenario.

Similarly, the impact of isocyanates on health has also gained much interest recently. Isocyanates are generated from thermal decomposition of urethanes, which are found in various forms in a building, e.g. as insulation, as upholstering material or in lacquers, and glue etc. It is also probable that isocyanates can be generated from nitrogen containing compounds in a vitiated fire as a result of incomplete combustion.

In the majority of fire situations, people are only exposed to sub-lethal levels of particles and isocyanates. The long-term effect can, however, be range from no effect or slight asthma to severe heart and/or respiratory malfunction.

The results obtained in this work demonstrate that it is possible to obtain life threatening conditions in fire smoke based on isocyanate concentrations, when the amount of both HCN and CO are still far from dangerous.

We also show in this report that for some materials, isocyanates tend to be enriched on the particle phase whereas for other materials, isocyanates are only found in the gas phase and not on the particles.

The main aim of this project has been to investigate the capability of various materials and products found in buildings to generate particles and isocyanates. Also, the amount of isocyanates absorbed on part of the respirable particle phase has been measured. Further, during the experiments other gaseous compounds (HCl, HCN, HF, CO, SO₂, ..) have been measured.

Eighteen standard building materials have been tested together with four different cables and two consumer products (a sofa and a mattresses). The majority of the experiments were conducted in small scale, in the cone calorimeter (*ISO 5660*). Single experiments were made according to *EN 13 823* (SBI), *ISO 9705* (Room-Corner) and *IMO A.800(19)*. Carbon fibre experiments were mainly performed in a small-scale tubular reactor according to DIN 53 436.

Particle distributions were measured using a low-pressure impactor and isocyanates were captured in an impinger bottle during the experiment. Subsequently isocyanates were analysed using a liquid chromatography-mass spectrometer (LC-MS) based technique. Other gaseous compounds were measured using an FTIR-instrument. The carbon fibre content was investigated optically (light microscope, SEM).

Sammanfattning

Förbränningsgenererade partiklars betydelse för vår miljö och hälsa har studerats relativt intensivt under senare år. Trots detta och trots de uppenbara hälsorisker och den miljöpåverkan som orsakas av (lokalt) mycket kraftiga partikelkoncentrationer från bränder i byggnader, har nästan ingenting gjorts för att undersöka denna typ av förbränningsgenererade partiklar.

I denna rapport redovisas utbyte samt mass- och antalsfördelningar av partiklar som skapats vid förbränning av olika 'typiska' byggnadsmaterial, eller material som återfinns i byggnader. I samband med projektet, testades även ett komposit material baserat på kolfiber och vi kunde visa att asbestliknande fibrer kan genereras vid en underventilerad förbränning.

Ett annat område som rönt mycket intresse, kanske främst i samband med arbetsmiljöstudier, är isocyanaters hälsopåverkan. Isocyanater har extremt låga miljögränsvärden och bildas bl.a. vid termisk nedbrytning av uretanbaserade material, vilka exempelvis återfinns i form av isoleringsmaterial, möbelstoppning, lack, lim, etc. Det är också troligt att isocyanat kan bildas ur kväveinnehållande material vid en ofullständig förbränning.

I de flesta brandsituationer där människor exponeras för isocyanater och partiklar från brandröken, är halterna långt ifrån dödliga. Emellertid kan långtidseffekter uppstå vilka kan vara allt ifrån en lätt astma till allvarigare respiratoriska problem och hjärt/kärl sjukdomar. I denna rapport visar vi att isocyanathalten i närheten av en brand kan vara direkt livshotande även när halterna av kolmonoxid och vätecyanid, -vilka brukar anses utgöra det största hotet i brandrök-, är långt ifrån farliga. Vi visar också i rapporten att isocyanat tenderar att anrikas på partikelfasen för vissa material medan andra ämnen endast producerar isocyanat till gasfasen.

Det huvudsakliga syftet med detta arbete har varit att undersöka partikel och isocyanat genererande egenskaper hos olika material och produkter. Dessutom har mängden partikelbunden isocyanat uppmätts. En del andra gaser (HCl, HCN, HF, CO, SO₂, ..) som genererades vid förbränningen uppmättes också.

Arton olika basmaterial har testats tillsammans med fyra olika kablar samt två konsumentprodukter (soffa och madrass). Huvuddelen av experimenten utfördes i liten skala genom förbränning i en konkalorimeter (*ISO 5660*). Enstaka experiment utfördes i större skala enligt *EN 13823* (SBI), *ISO 9705* ('Room-Corner') och *IMO A.800(19)*. Kolfiber materialet testades bl.a. i en tub reaktor enligt testmetoden DIN 53 436.

Partikelstorleksfördelning uppmättes med hjälp av en lågtrycksimpaktor. Isocyanathalter uppmättes genom att först absorbera ämnena i en impingerflaska med filter varefter lösningen (filtret placerades i en separat lösning) analyserades m h a vätskekromatografi samt mass-spektrometri. Andra gasformiga ämnen analyserades m h a ett FTIR instrument. Kolfiber materialet undersöktes optiskt med ljusmikroskop samt SEM.

1 Introduction

The environmental impact of airborne particles (‘aerosol’) has long been a major ecological and environmental concern¹, and in particular the antropogenic part of the particulate material has been studied. However, due to some alarming reports in the early 90’s², where statistically significant correlations were found between variations in airborne particulate matter and sickness/mortality within a population, this interest has also come to include the direct health impact of airborne particles^{3,4}. It has been estimated⁵ that almost half a miljon people die per year as a result of particles generated by car engines only. This number might be compared to the estimated deaths/year due to smoking, which is 3 million/year.

Generally speaking, all air in the atmosphere contains a certain amount of small particles; from $\sim 10^2/\text{cm}^3$ in maritime environments, to $\sim 10^6/\text{cm}^3$ in the air over large cities, and further to $\sim 10^9$ particles/ cm^3 in the flue gas from a boiler⁶ (before cleaning steps). Particle sizes range from the nanometer-scale up till several tens of a micron ($1\mu\text{m}=1.E-6$ m). A typical size distribution for urban air is shown in Figure 1⁷.

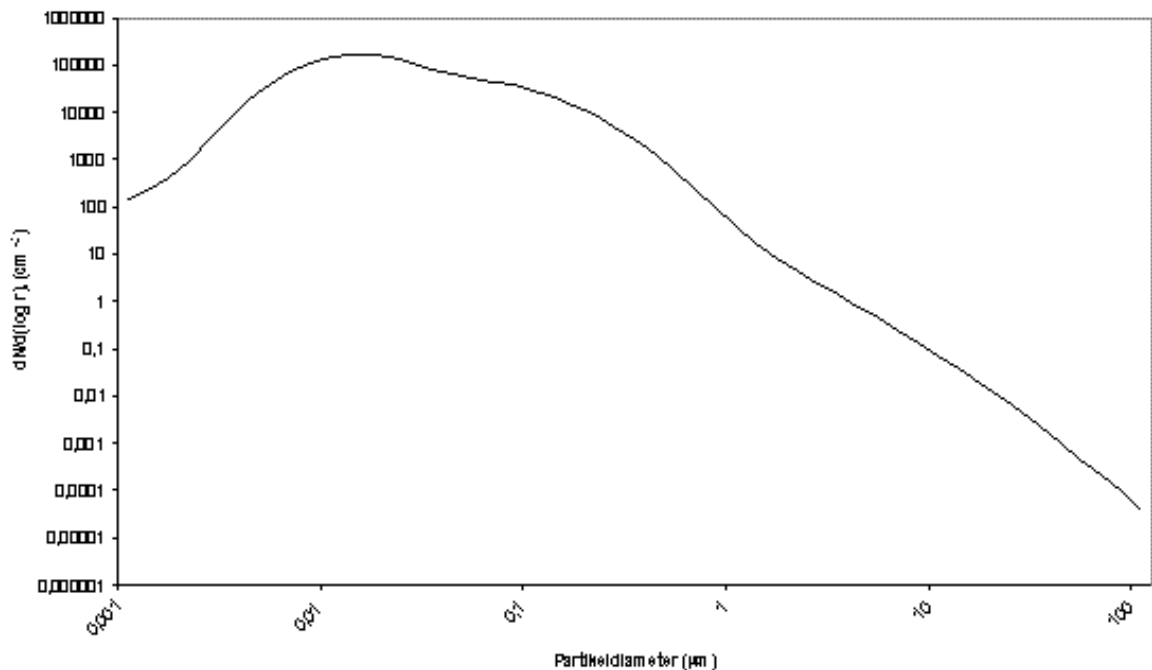


Figure 1 Typical particle number size distribution of urban air

Researchers have shown that the health effect is mainly related to the sub-micron sized fraction of the particles, i.e. to the particles having an aerodynamic diameterⁱ, d_p , less than one micron. Some even suggest that the real danger is related to the $d_p < 100$ nano meter (nm) fraction^{8,9}. Such small particles are generated in huge amounts in combustion processes, partly as a result of evaporation /condensation processes, partly from soot generation. Soot production is particularly high for a vitiated fire which is a common scenario in, for example, a compartment fire.

ⁱ The *aerodynamic diameter* is the diameter of a spherical particle with density= $1\text{g}/\text{cm}^3$, having the same terminal velocity as the particle studied. The particles, at least the larger ones, are in reality rarely spherical.

Another potential health-hazard related to the particles is the possibility for absorption and enrichment of various poisonous substances (metals, dioxines, HCl, ...) on the particle phase. Due to the huge number of particles in the smoke from a fire, there is a lot of available surface area and since the amount of ‘fine’ particles (aerodynamic diameter, d_p , of 100 nm or less) easily reaches⁶ $\sim 1E15$ particles/m³, the equivalent area will be 20-30 m² per m³ of gas. This estimation is based on the particles having a spherical shape. In real life this may not be the case, which means that the available surface area for absorption will be even larger. Also the amount of particles can be even higher.

Basically, particles having a diameter of less than 10 μm can be inhaled and the smaller the particle, the less probable it is that the defense system of the body will be able to prevent the material from reaching deep into the lung system. This is shown schematically in Figure 2. Figure 3 shows the probability for deposition of different particle sizes in different areas of the lung system¹⁰.

It seems likely that poisonous substances will have different impacts on the human body depending on whether they are inhaled as gaseous molecules or as molecules absorbed on a solid/liquid surface. The lung-molecule interaction depends on the physical and chemical context in which the interaction takes place. Also, the particle can provide a certain inertia to the adsorbed molecule that will influence where in the lung region the interaction will take place. In spite of this, there is not (to our knowledge) any particular health related limit values for substances found on the particle phase of an aerosol. Limit values are usually based on volumetric concentrations without regard for the different phases contained in that volume. The main reason for this is probably the general difficulties involved in estimating the health impact of particle-bound substances.

A substance that has been very much discussed in recent years is isocyanate. This is actually a collection of substances sharing the same functional group (-NCO). It is known to have an extremely low hygienic limit before injury. As an example, the substance toluene-2,4-diisocyanate (TDI), is given a health rating of 3 by NFPAⁱⁱ (The National Fire Protection Association), which translates into

‘Materials which upon short-term exposure could cause serious temporary or residual injury even though prompt medical treatment is given, including those requiring protection from all bodily contact’.

Isocyanates are known to be able to induce asthma in people having been exposed to even relatively small amounts. The substances are also known to have a very low limit value for creating direct life threatening conditions. NIOSHⁱⁱⁱ (National Institute for Occupational Safety and Health) provide an “immediately dangerous to life or health air concentration values (IDLHs)” of 2.5 ppm for TDI. For comparison, the IDLH given for HCN is 50 ppm and for CO 1200 ppm. Other isocyanates are usually considered to be as toxic as TDI.

Isocyanates are used for manufacturing polyurethanes (PUR) and also frequently used for glue manufacturing and in lacquers. The production volume per year of materials where this substance is used is large and increasing.

In this work, we will show results from several small scale combustion experiments in the Cone calorimeter, according to ISO 5660-1¹¹, and in a tubular furnace, according to DIN 53 436¹⁸. Results from one full scale, room-corner test (ISO 9705¹²), an intermediate

ⁱⁱ www.orcbs.msu.edu/chemical/nfpa/nfpa.html

ⁱⁱⁱ www.cdc.gov/niosh/idlh/idlh-1.html

scale test (SBI, EN 13283¹³) and a large scale test (IMO Resolution A.800(19)¹⁴) will also be reported. Different ‘typical’ materials from buildings were used for the small-scale experiments. In the tubular furnace and SBI test, carbon fibre laminates were burnt and in the Room-Corner test, a piece of upholstered furniture was used. The latter experiment went to flash over. In the large scale test a number of mattresses were burnt and staff involved in the experiment were tested to see if they had increased levels of isocyanate metabolites in their bodies.

The amount of particles were obtained using a DEKATI low pressure impactor that collects particles in the size range of 30 nm to 10 μm ^{iv}. Further, the amount of isocyanates was measured, both in the gas phase and in parts of the particle phase. This was accomplished using an impinger bottle, followed by a particle capturing filter. The isocyanate content was then analysed using an LC-MS technique. Other toxic gases in the flue gas (CO, HCN, HCl, etc) were measured on line using an FTIR instrument.

The Cone calorimeter test was used in order to conduct measurements based on a well known and well documented standardised fire test method. However, a limitation related to using this method is that the combustion in the standard configuration will be well ventilated. It is well known that in a vitiated fire a larger amount of particles and toxic combustion products are generated than in a well-ventilated fire. Another limitation in the investigation was that the dynamics of particle/gas generation were not studied. Particle and gas concentrations were measured over the entire experimental period, i.e. we did not differentiate between pyrolysis, fire and extinguishing periods. The main aim of this project has been to perform an initial scanning of different materials and products in order to get a general idea of particle and gaseous contents in the flue gas from common building materials and not to conduct an exhaustive investigation of the dynamics of such production.

^{iv} Particles larger than 10 μm will also be captured. If there is a risk of too much large particles that might lead to an ‘overload’ of the Impactor filters, a cyclone might be used for pre-treating the gas. However, this was not needed in the experiments performed during this project.

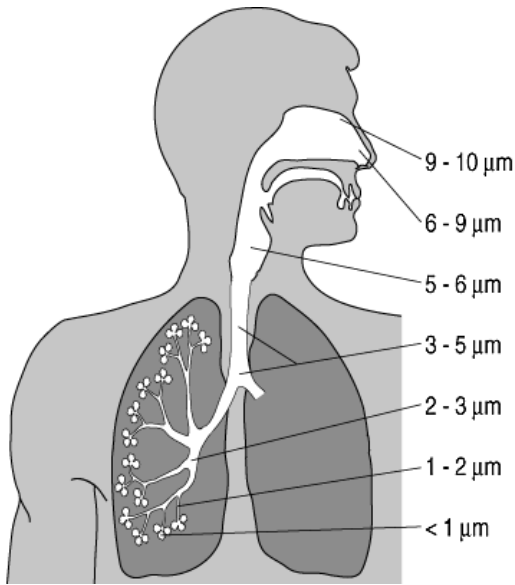


Figure 2 Particle deposition in respiratory system

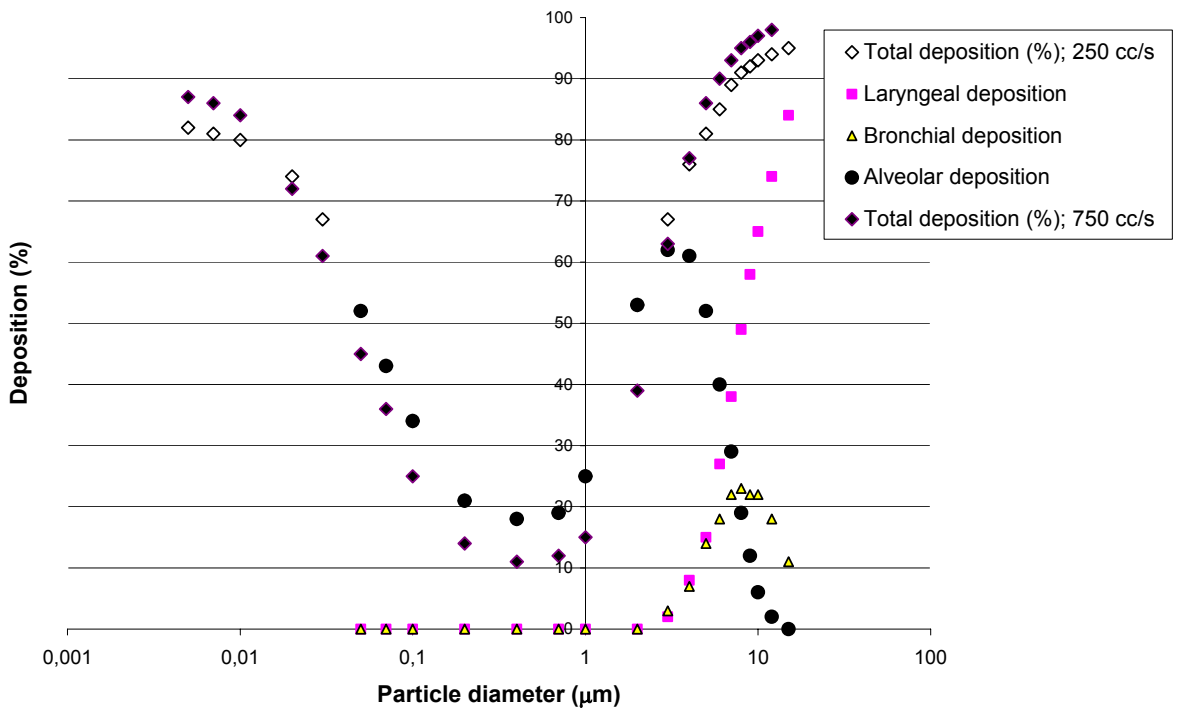


Figure 3 Deposition 'efficiency' of spherical particles with unit density ($1g/cm^3$) in respiratory tract¹⁰.

2 Materials tested

The main aim of this project has been to obtain a picture of the potential capacity for particle generation from different materials commonly found in buildings, and to investigate isocyanate production and phase distribution for these materials. Additionally, some cable materials have been tested in the small-scale experimental set-up since they are an important part of the overall fire hazard in buildings. A piece of upholstered furniture (a sofa) was tested in the room-corner test to get an idea of particle and isocyanate levels in a full scale fire, and a composite material (laminates of carbon fibre and vinyl ester resin) were tested in various fire scenarios. The main reason for including the latter material was to investigate if asbestos-like fibres could be generated from burning this material. Finally, isocyanates were measured in the air during a large-scale test and two people from the staff involved in the experiment were tested to see if they had been exposed to these substances.

In Table 1 the products used in this series of tests are listed.

Table 1 Materials and products investigated within the test program.

| Material | Comment | usage |
|-----------------------------|--|---|
| Glass fibre | insulation wool | building insulation |
| Mineral fibre | insulation wool | building insulation |
| Wood | Deal board | building construction |
| Bitumen | waterproofing membrane | building construction |
| Polystyrene | expanded polystyrene (EPS) | packaging, insulation, etc |
| Nitrile rubber | insulating material | tubing insulation |
| PVC | flooring material | surface lining |
| Fluoropolymer | pure pellet material | cable base material |
| Polyethylene | halogen free, fire retarded pellets | cable base material |
| FR4 laminate | brominated laminate | printed circuit board base material |
| Melamine | laminare | building construction |
| Wool | 92 % wool, 8 % polyamide | lining, clothes |
| Particle board | laminare | building base material |
| PUR | flexible foam | furniture upholstery |
| PUR | rigid foam | building insulation |
| PIR | rigid foam- polyisocyanurate (modified PUR) | building insulation |
| Plywood | laminare | room surface lining |
| Carbon fibre laminate | composite material, small and intermediate scale experiments | high performance vehicles, airplanes, etc |
| <i>Cable products:</i> | | |
| Polyethylene cable | halogen free, fire retarded cable | data cable |
| PVC cable | fire retarded cable | data cable |
| Fluoropolymer cable | high performance cable | data cable |
| PVC+fluoropolymer cables | 50% of each material | data cable |
| Optical cable | uses urethane acrylate based polymer | optical signal transport |
| <i>Real-scale products:</i> | | |
| Sofa | PUR upholstery; full scale experiment | furniture |
| Mattress | PUR; large scale experiment | furniture |

3 Experiments

The majority of the experiments were conducted using the Cone calorimeter (ISO 5660-1¹¹); the range of materials tested can be found in Table 1. In these experiments particulates, isocyanates and some selected inorganic gas species were measured. Further, a piece of upholstered furniture (a sofa which contained PUR foam) burnt in the Room-Corner enclosure (ISO 9705¹²) to investigate the particle and isocyanate levels in a full-scale fire.

The carbon fibre laminate was tested in different fire scenarios. These scenarios included the Cone calorimeter, the intermediate scale SBI test (EN 13581-1¹³), and a tubular furnace (DIN 53 436¹⁸). Fibre content of the gas must be investigated through inspection of particle geometries, e.g. by using an SEM. This was not done for the Cone calorimeter experiment where only the amount of particles was measured.

Since it was found in the small- and the full-scale experiments that the production of isocyanates in fires including PUR was substantial, it was decided to investigate the exposure of isocyanates on people from such a fire. The staff involved in a large-scale experimental series burning mattresses (IMO Resolution A.800(19)¹⁴), were tested to determine whether they had increased levels of isocyanate metabolites in their body after the test series. Furthermore, isocyanate measurements were conducted in the atmosphere at some key locations where staff stayed during the tests.

The experimental conditions for the Cone calorimeter experiments, the room experiment, and the experiments specific for the carbon fibre laminate are described in the following three subsections. Some results, specifically relating to microscopic investigation of fibres from the carbon laminate, can be found in this subsection, otherwise results are presented and discussed in the “Results and discussion” section.

Description of sampling and test conditions for the large-scale mattress test can be found in a separate section. The results from this investigation are discussed further there

3.1 Cone calorimeter experiments

The Cone calorimeter was used as a screening tool to investigate possible differences in particle production/distribution for a large number of materials, and to investigate the production of isocyanates and amines for these materials. In addition to these parameters a selected numbers of inorganic gases were measured, for most materials, using FTIR technique. The Cone calorimeter was selected as the fire model in this exploratory work due to its wide acceptance as a well-defined small-scale test method, and the ease for quantitative collection of smoke gases.

The tests were conducted according to ISO 5660-1¹¹; heat release rate (HRR), smoke production rate (SPR) and mass-loss were recorded. For the majority of materials only single tests were run. However, for a selected number of materials, multiple tests were conducted in order to investigate repeatability of the measurements. An irradiation level of 35 kW/m² from the cone heater was used in all experiments. The choice of 35 kW/m² was a trade-off between a lower value which possibly would have caused some material to pyrolyse only, and a higher value which might have provoked an unrealistically ‘clean’ burning behaviour

All tests conducted with the Cone calorimeter and details on the tests are given in Table 3. Note that the carbon fibre laminate material was tested in the cone using a vitiated atmosphere. This is further described in the next section.

Particles were sampled and size determined using a *DEKATI* low pressure impactor^v. A sub-flow of the smoke gases was led to the impactor from the horizontal duct of the Cone calorimeter at a position 61.5 cm from the centre of the sample. This sub-flow had a flow rate of 10 l min^{-1} , which together with the 10 mm diameter nozzle of the sampling probe (positioned in the centre of the duct and pointed in the direction towards the gas stream) resulted in iso-kinetic sampling conditions. The low pressure impactor measures airborne particles, size distribution in the size range $0.03 - 10 \text{ }\mu\text{m}$ (see footnote iv), with 13 channels by the means of pre-weighed impactor plates. Airborne particles are size classified according to their aerodynamic diameter in the cascade low pressure impactor. The sampled mass distribution within the 13 size ranges was determined gravimetrically after each test. The gravimetric determination was made using a calibrated analytical balance with a mass error less than $4 \text{ }\mu\text{g}$. The impactor plates were stored in a desiccator before weighing.

Isocyanates and amines were sampled using an impinger-filter sampling system¹⁵. This system samples airborne isocyanates in a 30 ml midget impinger bottle containing 10 ml reagent solution of 0.01 mol dm^{-3} DBA (D-n-butylamine) in toluene. A 13 mm glass fibre filter with a pore size of $0.3 \text{ }\mu\text{m}$ was placed in series after the impinger. After sampling, the filter was immediately placed in a test tube containing 10 ml of the DBA/toluene solution. It has been shown¹⁵ that large particles ($> 1.5 \text{ }\mu\text{m}$) are retained in the impinger solution, whereas smaller particles pass through the impinger solution and are collected by the filter. The filter is continuously impregnated by the reagent solution during sampling (the DBA/toluene solution is rather volatile), and particles in the size range $0.01 - 1.5 \text{ }\mu\text{m}$ are collected^{vi}.

The flow of gases extracted for the determination of isocyanates was sampled iso-kinetically. The sampling probe was positioned based on the same principles as the probe used for the particle sampling. The total flow rate for sampling of isocyanates was 2.0 l min^{-1} and the nozzle of the sampling probe had a diameter of 4 mm. The smoke gases were drawn through a 1.5 m heated sampling tube (4 mm i.d. PTFE, 150°C) and split to two impinger-filter samplers by means of two calibrated sampling pumps (1 l min^{-1} each). Approximately 0.2 m of the sampling tubing, closest to each impinger-filter sampler, was left unheated to cool the smoke gases somewhat before entering the impinger bottle, in order to avoid too great losses of the volatile absorption solution.

The collected isocyanate samples were subsequently analysed for isocyanates and amines. Analyses were conducted separately for the impinger solution and the filters. The analysis method was based on LC-MS technique and has previously been described by Karlsson et al.¹⁵. The individual species analysed and the specific quantification limits are shown below.

^v www.dekati.com/dlpi.shtml

^{vi} This is the size of particles that will pass the impinger flask.

Table 2 Isocyanate and amino-species measured in the experiments.

| Specie | Abbreviation | Quantification limit |
|---------------------------------------|--------------|----------------------|
| ISOCYANATES | | |
| 2,4-Toluene diisocyanate | 2,4-TDI | 0.005 µg |
| 2,6-Toluene diisocyanate | 2,6-TDI | 0.005 µg |
| 4,4-Methylenediphenyl isocyanate | 4,4-MDI | 0.005 µg |
| Hexamethyl diisocyanate | HDI | 0.005 µg |
| Phenyl isocyanate | PHI | 0.01 µg |
| Methyl isocyanate | MIC | 0.01 µg |
| Ethyl isocyanate | EIC | 0.01 µg |
| Propyl isocyanate | PIC | 0.01 µg |
| Isoforon diisocyanate | IPDI | 0.005 µg |
| Isocyanate acid | ICA | 0.05 µg |
| AMINOISOCYANATES | | |
| 2,4-Toluene aminoisocyanate | 2,4-TAI | 0.01 µg |
| 2,6-Toluene aminoisocyanate | 2,6-TAI | 0.01 µg |
| 4,2-Toluene aminoisocyanate | 4,2-TAI | 0.01 µg |
| Hexamethylene aminoisocyanat | HAI | 0.01 µg |
| 4,4-Methylenediphenyl aminoisocyanate | 4,4-MAI | 0.01 µg |
| AMINES | | |
| 2,4-Toluenediamine | 2,4-TDA | 0.05 µg |
| 2,6-Toluenediamine | 2,6-TDA | 0.2 µg |
| 4,4-Methylenedianiline | 4,4-MDA | 0.1 µg |
| 1,6-Hexamethylenediamine | 1,6-HDA | 0.1 µg |

Time resolved measurements of the concentration levels of various inorganic gases in the exhaust duct were obtained using a BOMEM MB 100 FTIR spectrometer. The analyser was equipped with a heated gas cell (volume = 0.92 l, path-length = 4.8 m, temperature = 150°C). A spectral resolution of 4 cm⁻¹ was used, with 4 averaged spectra (based on 3 full scans) recorded per minute. The smoke gases were continuously drawn to the FTIR with a sampling rate of 4 l min⁻¹ using a probe with a filter mounted in the exhaust duct of the Cone calorimeter. Both the filter and the gas sampling line (4 mm i.d. PTFE) were heated to 180 °C. The proper function of the FTIR equipment was verified by measurement of a calibration gas. The FTIR data (spectra) was quantitatively evaluated for a selected number of gas species. These gases were: carbon monoxide (CO), hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen fluoride (HF), hydrogen cyanide (HCN), nitrogen monoxide (NO), nitrogen dioxide (NO₂), ammonia (NH₃) and sulphur dioxide (SO₂).

The sampling of particles and isocyanates, normally covered the complete test-period (i.e. until 2 minutes after extinction, or a total of 10-15 minutes in cases where the material did not ignite). Hence, the sampling time differed considerably between the different materials (data can be found in Table 3). However, as both methods were accumulating sampling methods, it was decided that this would be the best strategy in order to include all stages in the combustion of the material. The time for particle collection was, however, occasionally shortened due to the risk of overloading the filters of the impactor.

Similarly the isocyanate sampling time was sometimes shortened when parts of the sampling equipment became clogged by soot. For the measurements of inorganic gases with FTIR, the time resolved measurement covered the complete test period.

In a majority of the experiments, flaming combustion took place within a few seconds, but for some cases, pyrolysis of the material was the only visible result of the heating. The time for the particles to reach the sampling equipment must be considered 'short'; once the particle reaches the Cone calorimeter exhaust duct inlet, the volume flow is such that transportation is achieved in less than a second (see footnote xi). Since the inlet is situated close to the sample, the total age of sampled particles will not be more than maximum 2 to 3 seconds, probably less for most cases.

Table 3 Test and measurement data for the Cone calorimeter experiments. Total sampling/measurement times are given for the analysers.

| Material | Number of tests | Duration of test (min:s) | Time for ignition (min:s) | Impactor (min:s) | Isocyanates (min:s) | FTIR (min:s) |
|---------------------------|------------------------|---------------------------------|----------------------------------|-------------------------|----------------------------|---------------------|
| Carbon fibre laminate* | 1 | 7:11 | 0:49 | 5:00 | - | - |
| Glass fibre insulation | 2 | 15:00 | - | 15:00 | 15:00 | - |
| | | 15:00 | - | - | 15:00 | 15:00 |
| Mineral fibre insulation | 2 | 15:00 | - | 15:00 | 15:00 | - |
| | | 15:00 | - | - | 15:00 | 15:00 |
| Wood | 1 | 12:17 | 2:17 | 12:17 | 12:17 | - |
| Bitumen | 1 | 5:46 | 0:46 | 5:46 | 5:46 | - |
| Polystyrene | 1 | 10:00 | - | 10:00 | 10:00 | - |
| Nitrile rubber | 1 | 4:57 | 0:01 | 4:57 | 4:57 | 4:57 |
| PVC | 1 | 4:54 | 0:24 | 4:54 | 4:54 | 4:54 |
| Fluoropolymer | 1 | 10:00 | - | 10:00 | 10:00 | 10:00 |
| FR4 laminate | 1 | 2:07 | 0:27 | 2:07 | 2:07 | 2:07 |
| Melamine | 1 | 3:50 | 0:33 | 3:50 | 3:50 | 3:50 |
| Wool | 2 | 2:58 | 0:15 | 2:58 | 2:58 | 2:58 |
| | | 7:10 | 0:30 | - | 7:10 | 7:10 |
| Particle board | 3 | 11:05 | 1:05 | 11:05 | 11:05 | 11:05 |
| | | 13:40 | 1:06 | 13:40 | 13:40 | 13:40 |
| | | 14:30 | 1:02 | 14:30 | 14:30 | 14:30 |
| PUR (flexible) | 3 | 3:19 | 0:02 | 3:19 | 3:19 | 3:19 |
| | | 3:47 | 0:02 | - | 3:47 | 3:47 |
| | | 3:17 | 0:04 | - | 3:17 | 3:17 |
| PUR (rigid) | 1 | 5:31 | 0:01 | - | 5:31 | 5:31 |
| PIR (rigid) | 1 | 9:01 | 0:01 | - | 9:01 | 9:01 |
| Plywood | 1 | 9:42 | 1:00 | - | 9:42 | 9:42 |
| Polyethylen pellets | 1 | 11:03 | 1:01 | 11:03 | 7:30/10:00 | 11:03 |
| Polyethylen cable | 1 | 9:50 | 1:47 | 9:20 | 9:20 | 9:50 |
| PVC+ Fluoropolymer cables | 1 | 16:17 | 1:17 | 10:00 | 7:20/5:40 | 16:17 |
| PVC cable | 1 | 12:50 | 1:00 | 12:50 | 7:05/5:55 | 12:50 |
| Fluoropolymer cable | 1 | 10:00 | - | 10:00 | 10:00 | 10:00 |
| Optical cable | 1 | 6:55 | 1:32 | 6:55 | 3:30/3:40 | 6:55 |

* The carbon fibre laminate was tested in a vitiated atmosphere.

3.2 Room experiment with sofa

A ‘standard’ sofa was placed in the back of the enclosure of the ISO 9705 Room test. The sofa was composed mainly of polymers (PUR, styrene,..) and wood material (particle board, plywood,..). Ignition source was a candle that was mounted in the centre of the furniture. Initially the fire grew quite slowly, visible smoke production started at ~5 minutes and flashover (~1 MW) was reached approximately 10 minutes after ignition. Particulates as well as isocyanates were measured in this experiment. FTIR was not used for measurements of inorganic fire gases. However, CO₂ and CO was measured with an NDIR analyser. Particulate material was measured using the DEKATI low pressure impactor previously described. The iso-kinetic sampling probe was located approximately 6 m after the exhaust duct inlet, which means a time delay of ~0.3 s from the inlet. Time delay from the fire to the inlet varies as a function of the smoke plume volume but the major part of the particles are generated close to flashover and in this instance, the volume flow leaving the opening of the Room-Corner might be estimated to be some hundred litres/minute. Since the smoke layer at this point in the experiment occupies roughly half the enclosure volume, ~10 m³, the average age of the particles leaving the room could be 10-30 seconds, assuming that the smoke volume can be represented as a ‘well-stirred tank reactor’^{vii}. This means a longer time given for the particles to agglomerate than in the Cone calorimeter or the SBI discussed below. However, the shape of the particle distribution curve is very similar to the other experimental curves, indicating that the extra time given to the aerosol in this experiment is not enough for substantial particle agglomeration to take place.

The sampling point for isocyanates was placed at approximately the same location as the particle sampling. The sampling of isocyanates was, however, not conducted iso-kinetically in this test. Sampling and analysis of isocyanates was, in all other respects, identical to that previously described for the Cone calorimeter tests.

3.3 Experiments with carbon fibre laminate

Composite fibrous material has been suspected of being able to create particles when burning, that have shapes resembling asbestos particles (long and thin) and hence the potential to create particles that are carcinogenic. In order to test this hypothesis, we included a carbon-/glass-fibre composite material in the experimental series. The polymer used for manufacturing of the laminate board was a vinyl ester. In the various experiments with the carbon composite, only particulates were measured. Results regarding microscopic investigation of sampled particles are discussed here, whereas the results on particle size distribution are discussed in connection with the results from the other materials tested.

3.3.1 Cone calorimeter experiments

The carbon fibre laminate was tested in the Cone calorimeter with a reduced oxygen atmosphere in order to obtain vitiated conditions. This should in theory produce higher amounts of soot than would a well-ventilated scenario¹⁶. An airtight stainless steel box, specially constructed for this purpose, was fitted to the Cone calorimeter to enclose the balance/sample holder and the cone heater. By using this arrangement an atmosphere containing 16% oxygen was created by flushing the box continuously with a mixture of air and nitrogen. Particulate material was measured using the DEKATI low pressure

^{vii} ‘Tank’ volume divided by smoke volume flow provides time estimate

impactor as described above. Samples for microscopic investigation were however not collected. Additional information regarding the test can be found in Table 3.

Although a reduced oxygen atmosphere was established around the sample, which prevented the pyrolysis gases from effective combustion within the box, the unburned gases had access to ambient air above the cone heater, which created “after-burning” of the gases at this point. Thus the actual combustion conditions were not as vitiated as could be anticipated from the reduced oxygen atmosphere. The results from the impactor measurements are given in the section below. No ‘visual’ inspection of fibre content was performed in this test.

3.3.2 SBI experiment

Two pieces of composite material boards (1500×500×4 mm, 1500×1000×4 mm) were mounted in the SBI equipment and the experiment was performed according to EN 13823-1¹³. Particulate material was measured using the DEKATI low pressure impactor previously described, approximately 10 m after the exhaust duct inlet, which implies a time delay of ~1.3 s from the inlet. Estimating the time for the gas to be transported from the board to the inlet of the exhaust duct to be ~1 s, the age of the particulate material will be ~2.5 s at the measuring point. The impactor samples were not suitable for direct inspection of particle geometry. Instead, a filter (FEMPORE, Millipore) capable of retaining particles >0.4 µm was used to obtain particles that were subsequently investigated using microscopes (light and SEM). The sampling position was ~1.5 m downstream of the impactor. Samples for the investigation were also taken from the residues of the composite boards after the experiment had finished, by pressing an adhesive tape against the charred material.

The samples taken for microscopic investigation did not show any sign of fibres resembling the asbestos type. A few glass fibres were found but they were all considered to be too large for creating any health hazard; the smallest were >3µm thick and >20 µm in length. However, it must be emphasized (and it is further demonstrated in the small-scale test below) that the results are not conclusive and do not rule out the possibility of generating dangerous fibrous material from carbon composite material.

From a fire safety point of view, the test of the carbon fibre in the SBI indicates that it could be classified as a ‘D’-material, according to the European classification system for surface linings¹⁷. The results from the impactor measurements are given in the section below.

3.3.3 Tubular furnace tests

In order to create experimental conditions with a controlled oxygen deficient atmosphere, two tests were conducted using a tubular furnace with a moving circular furnace element. The tubular furnace test apparatus was constructed according to the DIN-53 436 standard¹⁸. The only difference from the specifications in the standard was that the length of the furnace was 170 mm, instead of the 100±1 mm specified. The quartz glass tube was continuously flushed with air containing 16% oxygen at a flow rate of 3.5 l min⁻¹. A sub-flow of 2.5 l min⁻¹ was drawn through a 5 µm PTFE membrane filter (with a glass fiber filter as a backup) at the end of the quartz tube to collect particulates. The two tests were conducted with a furnace temperature of 500°C and 700°C respectively. The sample weights (in grams) were 30.2/30.8 before and 21.1/19.5 after the tests respectively. The

length of the sample was 400 mm, which with a furnace speed^{viii} of 10 mm min⁻¹ and a furnace length of 170 mm led to a total time for the tests of ~60 minutes.

In the first test with a furnace temperature of 500°C no ignition of the sample could be observed. A sticky whitish condensate could be observed on the walls of the quartz tube and similar material was found on the membrane filter, where it was difficult to distinguish any particulate material. In the 700°C experiment, the sample ignited after ~5 minutes of experimental time and a dense smoke was then produced. The filter was covered with a thick layer of particulates and in the subsequent inspection of the sample using SEM (Scanning Electronic Microscopy), fibres with a high carbon content was found. The majority of these fibres where 0.1-1 µm thick and more than 20 µm long, i.e. they are to be considered as potentially dangerous to human health. An SEM picture from the sample is given in Figure 4.

It must be emphasized that these findings come from a single experiment but they indicate that this kind of composite material is potentially dangerous as it might produce asbestos resembling fibres given the ‘right’ combustion circumstances. A parametric study of this phenomenon is underway and will be reported in future work.

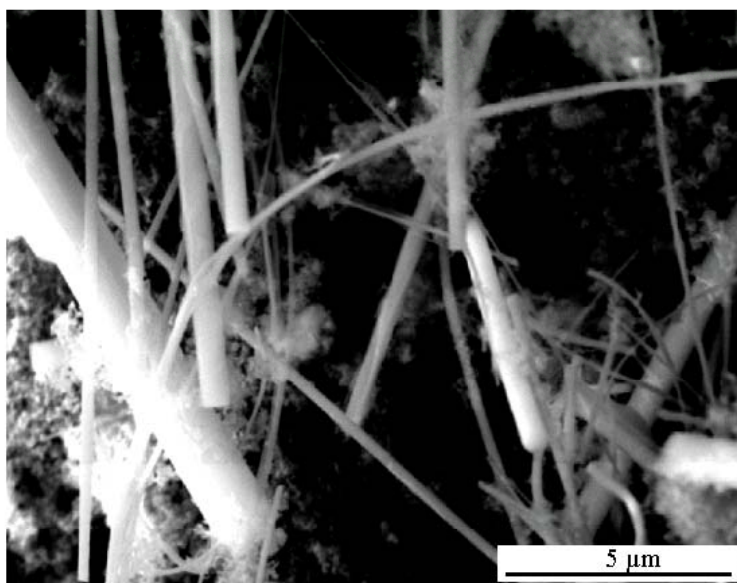


Figure 4 Fibrous carbon material

^{viii} The 170 mm furnace sweeps the sample, starting in front of it and ending when the furnace has moved, in a counter gas flow direction, so that the sample is fully visible again.

4 Results and discussion

The main experimental activity in this project was based on using the small-scale Cone calorimeter. Oxidation of the 100 cm² sized sample material was initiated by a 35 kW/m² irradiation. In a majority of the experiments, flaming combustion took place within a few seconds but for some materials, pyrolysis was the only visible result of the heating. However, this was enough to produce visible smoke and large amounts of particles. Indeed, materials that are not easily to ignite often have a higher potential for creating large amounts of smoke.

In all of the experiments, measurements were made over the entire experimental period, i.e. during the initial pyrolysis period as well as during the flaming combustion and burnout phase. It could be argued that it would have been a better principle to concentrate on one of these phenomena but the main target has been to get a general picture of particle concentrations in smoke and to capture the tendency for different materials to generate isocyanates and other gaseous components.

4.1 Particles

The particles were collected using a low pressure Impactor where the amount of material is obtained gravimetrically. In Figure 5 the mass distribution of particles obtained in all experiments is shown.

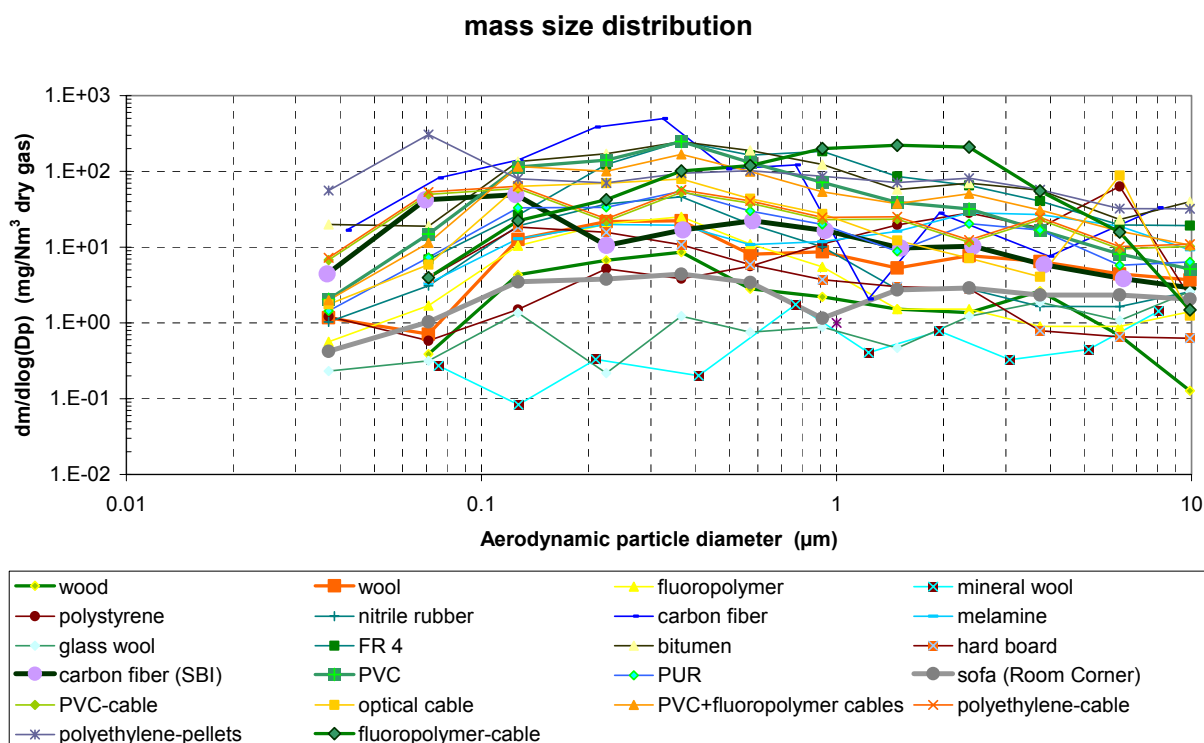


Figure 5 Particulate mass size distributions; logarithmic axes

Note that both axes are logarithmically scaled^{ix}. The particular formats used in the diagram are related to the need to describe mass distribution of particles varying in size by several orders of magnitude. Note further that the figure represents averaged (over the experimental time) mass distribution per normal m³ of gas. The concentration is, therefore, related to the dilution obtained in the particular experimental set-up, and it is not completely correct to compare values obtained in the Cone calorimeter with medium (SBI) and full-scale (Room-Corner) experiments. However, the comparison is relevant in order to demonstrate the similar shape of the graphs. It can be seen that there is a general trend of obtaining a maximum in the mass distribution around 0.1-0.3 μm. This is more clearly distinguishable in Figure 15-Figure 18 in the Appendix. One exception to this kind of distribution is the fluoropolymer based cable that has a maximum just above 1 μm.

All Cone calorimeter experiments, except when the Carbon fibre material was used, were based on the ISO 5660-1¹¹ standard. When the Carbon fibre laminate was tested, the samples were submitted to a reduced oxygen content (16%) in order to obtain vitiated pyrolysis conditions. This should, in theory, produce higher amounts of soot than a well-ventilated scenario¹⁹. Figure 15-Figure 18 (note the non-logarithmic scale on the y-axis) shows Figure 5 resolved into four different mass concentration classes and it can be observed that the highest particle concentration is indeed obtained for the carbon fibre experiment. However, the high carbon content of the laminate in itself indicates the possibility of a high soot and particle production even with a normal oxygen atmosphere present. This is also seen from the SBI Carbon fibre experiment (Figure 5 and Figure 16).

Bitumen is another ‘efficient’ particle producer with high carbon/asphalt content that also belongs to the ‘top’ group shown in Figure 15. The rest of this group consists of flame retarded material (Polyethylene, PVC, FR4) or samples that mainly were pyrolysed in the Cone calorimeter test (fluoropolymer based cable), i.e. no ignition took place.

Most of the tested materials were measured only once since we wanted a quick screening of many materials. However, a tripple experiment was performed on the particle board to test repeatability. The results are shown in Figure 6 where it can be seen that repeatability is ‘quite’ good.

To get a picture on the *number* of particles obtained in Figure 5, an assumed density must be used together with the assumed particle shape. Using the density on which the aerodynamic (see footnote i) particle diameter is based (1g/cm³) and assuming sphericity of the particles, the number-mapping of the mass distributions shown in Figure 5 is given by Figure 7. Obviously the density will vary depending on the particulate material but also depending on the particle size since the size relates to the shape. The smaller particles are more likely to be spherical while the larger ones might be very irregular as they often consists of an agglomeration of smaller particles. A correct density is therefore in reality not easily found for the entire spectrum of particle sizes. However, even if the real densities were several tens of procent different from the assumed value, the number distributions shown in Figure 7 would still be a relevant measure of the quantity of

^{ix} The diagram actually represents a bar graph and each point signifies a collection of particulate material for a size class i , defined by $\Delta d_p^i = (d_{p-\max}^i - d_{p-\min}^i)$, having the geometrical mean valued diameter given by the x-coordinate. The y-coordinate shows the obtained mass, Δm^i , for the class i , divided by the logarithm of that size fraction, i.e. by the ‘bar width’ in the logarithmic diagram, in order to obtain $\frac{\Delta m^i}{\log(\Delta d_p^i)} \approx \frac{dm^i}{d \log(dp_i)}$

particles generated, as the main cause for the large number concentration is related to the smallness of the particles^x and not so much to their densities. The number distribution shown is differentiated into 4 different pictures in Figure 19-Figure 22, based on the mass size distributions shown in Figure 15-Figure 18.

One interesting feature of the number distributions shown in Figure 7 is that they are all ‘mono-modal’ in character, i.e. there is only one distribution maxima for each curve, all located close to the minimum particle size. This is probably due to the short distance in time between the aerosol generation and the measuring point. For all three experimental set-ups where particles were collected, the samples were taken just a few seconds from the fire itself. It is difficult to give an exact measure of the time necessary for the particle to move from the generation spot to the exhaust duct since it depends on the smoke plume buoyancy, i.e. it depends on the HRR. However, the time should not be more than just a couple of seconds in the SBI and probably less for the cone calorimeter^{xi}. In the Room-Corner experiment, the particles might be older (~10-20 s) before reaching the exhaust duct inlet.

Once the particle is in the exhaust duct, the time to reach the measuring spot was below 1 second in the cone calorimeter, and below 1.5 seconds in the Room-Corner and SBI experiment. The short period before sampling will not allow any significant agglomeration of particles to take place²⁰.

The smaller the particle, the faster will be its diffusion induced velocity and the more likely it is that it will collide with other particles and agglomerate into larger clusters. The maxima for an ‘older’ aerosol is often located between 0.1 and 1 μm , since this particle diameter is large enough to have a low diffusional speed but also small enough to resist inertial forces. The latter statement is nicely pictured as a minimum in total lung deposition ‘efficiency’ for these particle sizes in Figure 3.

When comparing figures 1 and 8, it is important to consider that the atmospheric aerosol in Figure 1 contains much material that is different in nature to the combustion based, e.g. dust, inorganic salts, pollen, etc. Frequently, atmospheric aerosols exhibit a bi-modal distribution, i.e. demonstrate a distribution with two maxima, one sub- and one super-micron (multi-modal distributions are also reported¹⁹). The latter maximum stems from sources such as dust, salt and pollen while the former mainly is agglomerates of very small particles, a majority of which are generated from combustion sources.

It is important to note that the measurements reported in this paper all are averages over the experimental times. The effect of this is particularly important for the larger scales, e.g. the Room-Corner experiment, where almost all particulate material in reality is obtained close to the flash-over situation, which only constitutes a fraction of the total measurement time (~11 min for our case), i.e. for a short period of time the particle concentration is very high.

Another way to visualize the potency for particle generation from different materials, is to calculate the particulate ‘yield’, i.e. to relate the mass of the particulate phase in the smoke plume to the total mass loss of the experimental sample. The results from such relations are shown in Figure 8. Total particulate mass in the Cone Calorimeter exhaust

^x The number of particles is proportional to d_p^3

^{xi} Average linear flow speed in the Cone calorimeter exhaust duct is almost 2.5 m/s. In the SBI and Room-Corner it is ~7.8 and ~20 m/s respectively.

duct is calculated based on the impactor mass measurement^{xii} and the measured sample weight loss during the experiment.

It can be seen when comparing to other investigations that the yields shown in Figure 8 are of the same order of magnitude as the reported ones. The polyethylene ('Casico') material has previously been reported to provide ~3% particulate yield in the Cone Calorimeter²¹ (3.5% in Figure 8) and the yield for wood given in Figure 8, ~0.25%, might be compared to the amount reported for particulate material exhausted from an open fire place, ~0.6-1.6 %¹⁹ (the min/max depends on the wood-type). It is reasonable that burning of a dry ideal piece of wood under well-ventilated conditions in a Cone Calorimeter may provide somewhat better burning conditions, i.e. somewhat less particulate yield than would an open fire place.

Maximum particulate yield is obtained for the materials that do not burn well because of flame retardants. The polystyrene used is an exception to this as it is not flame retarded but did produce a large amount of particulate material. This is due to the presence of the styrene molecule (an aromatic species) in the polymer backbone. When polystyrene pyrolyses large amounts of aromatic molecules are produced providing the building blocks for soot formation and the basis for particle formation. Lowest yields are obtained for the materials that burn well, such as wood and particle board.

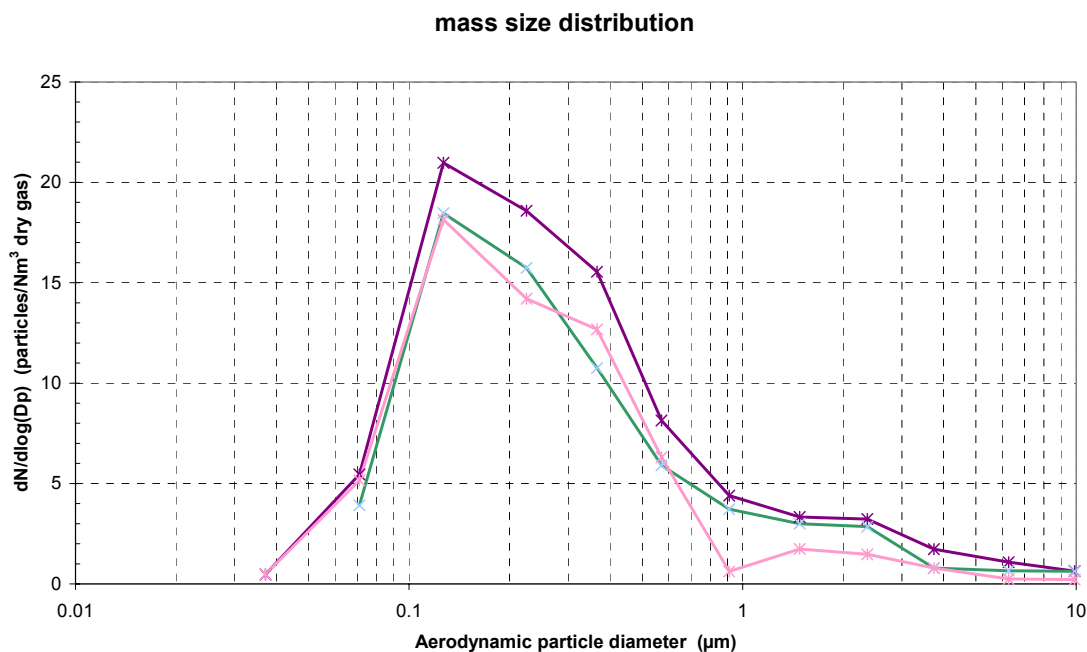


Figure 6 Multiple particle board measurements made to demonstrate repeatability.

^{xii} The total mass obtained this way might be misleading if the Impactor plates are over-loaded. However, during the experiments a heavy smoke production was compensated by a shortened time for exposure in order to avoid overloading.

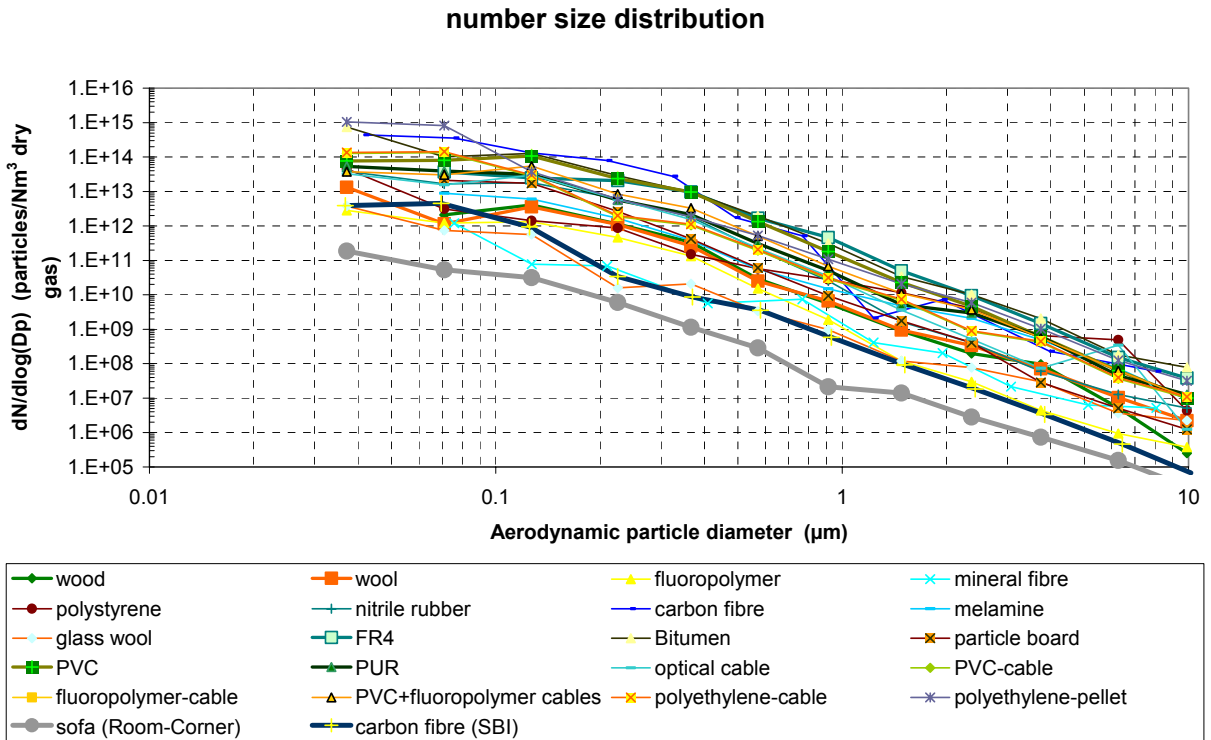


Figure 7 Number size distribution obtained by 'mapping' of particulate mass measurements.

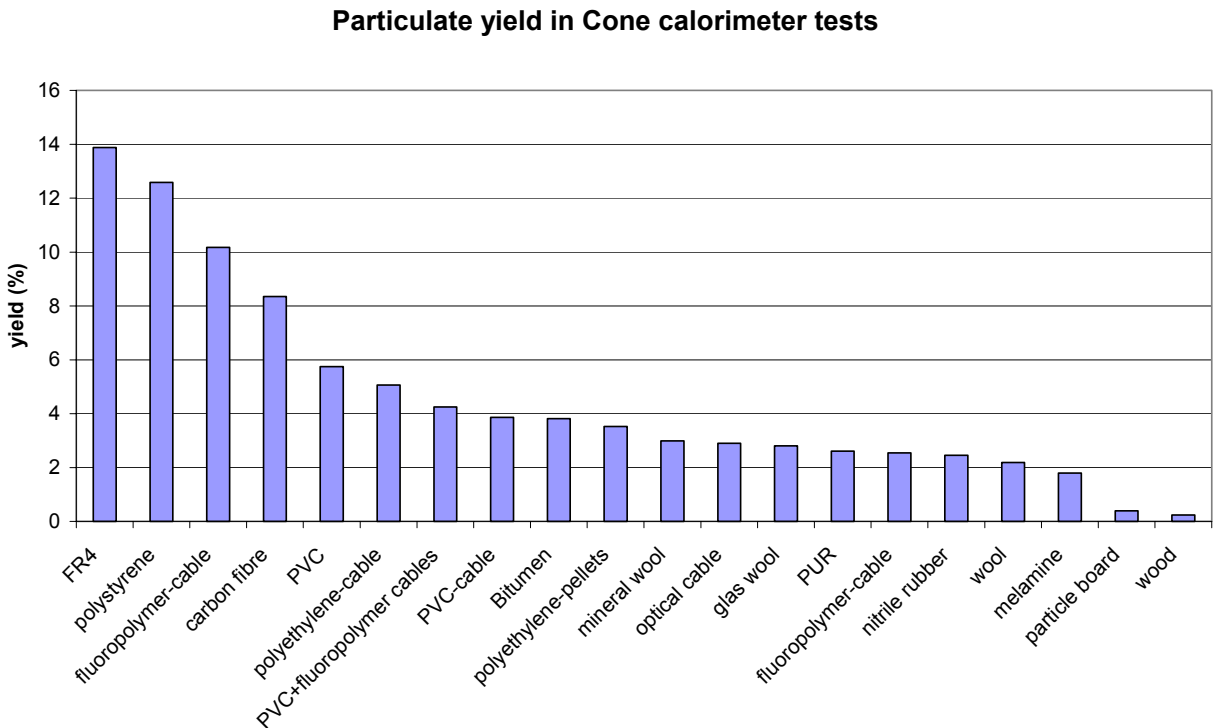


Figure 8 Yield obtained from Impactor and sample mass loss measurements

4.2 Isocyanates

Very little work has been conducted previously on the generation of isocyanates in flaming combustion, which is surprising, considering the high potential for damage even from small amounts of isocyanates. To our knowledge, the only available data is in a report made by the Swedish Rescue Service Agency regarding the isocyanate concentrations from car and shipboard fires²².

In this project, isocyanates were found in the smoke gases from all nitrogen-containing materials tested. Somewhat unexpectedly, however, isocyanates were also found from the cable products and e.g. bitumen and the PVC-carpet. The only materials that did not produce any isocyanates were the polystyrene and the pure fluoropolymer. These two materials (if chemically clean) have, however, very low potential to produce isocyanates as they have no nitrogen in their chemical structure. Further, considerable concentrations of isocyanates were found in the smoke gases from the room test with the sofa. Amines and amine-isocyanates were generally found in very low concentrations or not detected, with the exception of the PUR foam products, which produced significant amounts.

The total concentration (gas phase and particle bound) of isocyanates for all tests conducted in the Cone calorimeter can be found in Figure 14. The results presented in this figure are averaged results, including the results of the parallel sampling conducted, and multiple tests if conducted. Further, mass yields of total isocyanates based on the mass-loss of the material during the tests are presented in Table 4. Information regarding the portion of the isocyanates bound to particles can also be found in this table.

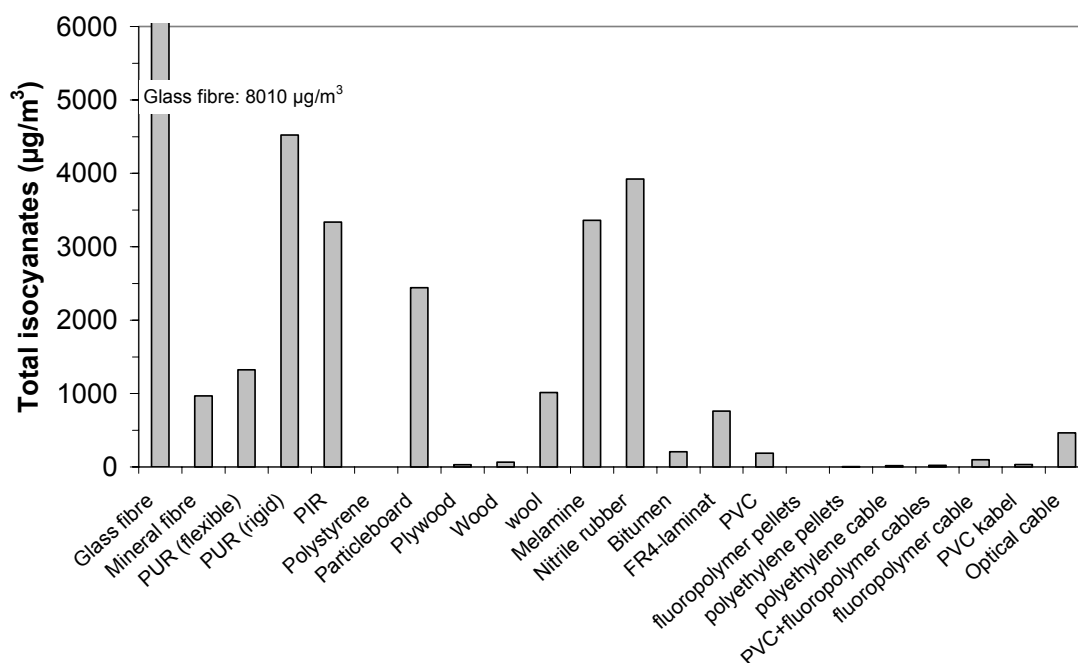


Figure 9 Total isocyanate concentrations in the Cone calorimeter tests

Blank tests were run on four occasions during the test series to track any contamination of the sampling/analysis system. In these tests a propane burner heated the Cone calorimeter system to create temperature and flow conditions mimicking a real tests. Isocyanates were found (in concentrations close to the quantification limit) in only one of these tests. Further, the lack of isocyanates for polystyrene and the fluoropolymer (materials with no nitrogen) indicates that the risk of contamination or misleading analysis results is low.

The deviation between the two parallel samples taken in each test was generally low. The deviation for multiple tests was higher, but generally satisfying for the purpose of this screening work. The individual results for the multiple tests conducted with some selected materials can be found in Figure 10. It can be seen from this figure that e.g. the first test with PUR (flexible) deviates significantly. We have, however, not been able to find any abnormalities in this test to explain the low result. The deviation between the results for the Wool is due to the fact that twice the amount of material was used in the second test to achieve a longer period of burning.

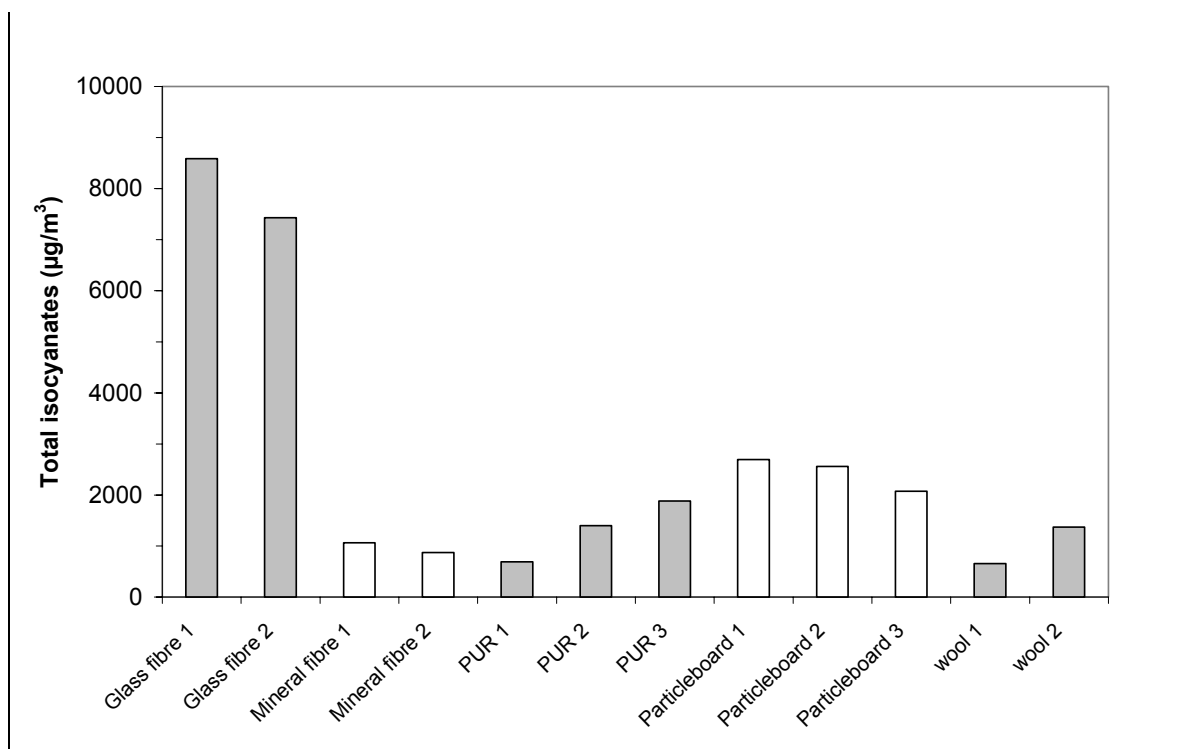


Figure 10 Isocyanate concentrations from repetitive tests in the Cone calorimeter.

It can be seen from Figure 9 that Glass fibre insulation gave the highest concentrations of all materials tested. The types of isocyanates found from the Glass fibre insulation were principally ICA and MIC. Similarly, significant amounts of ICA and MIC were found from the mineral fibre insulation. ICA was the dominating species for both materials. The binder in these materials is often cured phenol-formaldehyde-urea that preferably dissociates to isocyanates if heated. The findings of high concentrations of ICA and MIC correlate well with what has previously been reported from heating tests with mineral wool using a tube furnace¹⁵. In these tests up to 5% of the total mass was emitted as ICA and 1% as MIC. In our tests with the Mineral fibre insulation in the Cone calorimeter, approximately 3% of the total mass was emitted as ICA and 0.5% as MIC. The yield calculated for the Mineral fibre insulation is, however, somewhat uncertain as the mass-loss from this material was very low (approximately 0.5 g). The yields from the Glass

fibre insulation were, however, significantly higher, with an ICA yield of 6.8% and a MIC yield of 1.4%.

High concentrations of isocyanates were found from the polyurethane products tested as could be expected. Polyurethanes are produced by reacting isocyanates with a polyol, such as polyether, to form a flexible or a rigid polymeric product. TDI is used for the production of flexible PUR foam, elastomers and coatings, while pMDI (poly) is used for the production of rigid PUR foam. PIR foam is an improved type of rigid PUR. Different catalysts are used in the reaction, and the proportion of MDI is much greater than for PUR. Polyester derived Polyol is used in place of polyether. The reaction is achieved at higher temperatures, which enables some of the MDI to react with itself, creating strong Isocyanurate linkages in the molecular structure. These linkages are much stronger than the normal urethane linkages in PUR foam, and they are more difficult to ‘break’, making the foam chemically more stable.

The highest concentrations from the PUR foams were found from the two rigid foams. The PIR foam showed the highest yields, which can be seen in Figure 11. Both rigid PUR and PIR predominately emitted ICA and PHI; only low amounts of MDI were found. ICA (isocyanate acid) can be considered as the “final” breakdown product of the isocyanates in the polyurethane chain structure, whereas PHI (phenyl isocyanate) must be an intermediate product from the breakdown of MDI (methylenediphenyl isocyanate), the isocyanate used for production of a rigid PUR product. A more varied mix of isocyanates was found from the flexible PUR foam, were ICA, 2,4-TDI and 2,6-TDI were found in the highest amounts. This makes sense as TDI is used for the production of flexible PUR foams.

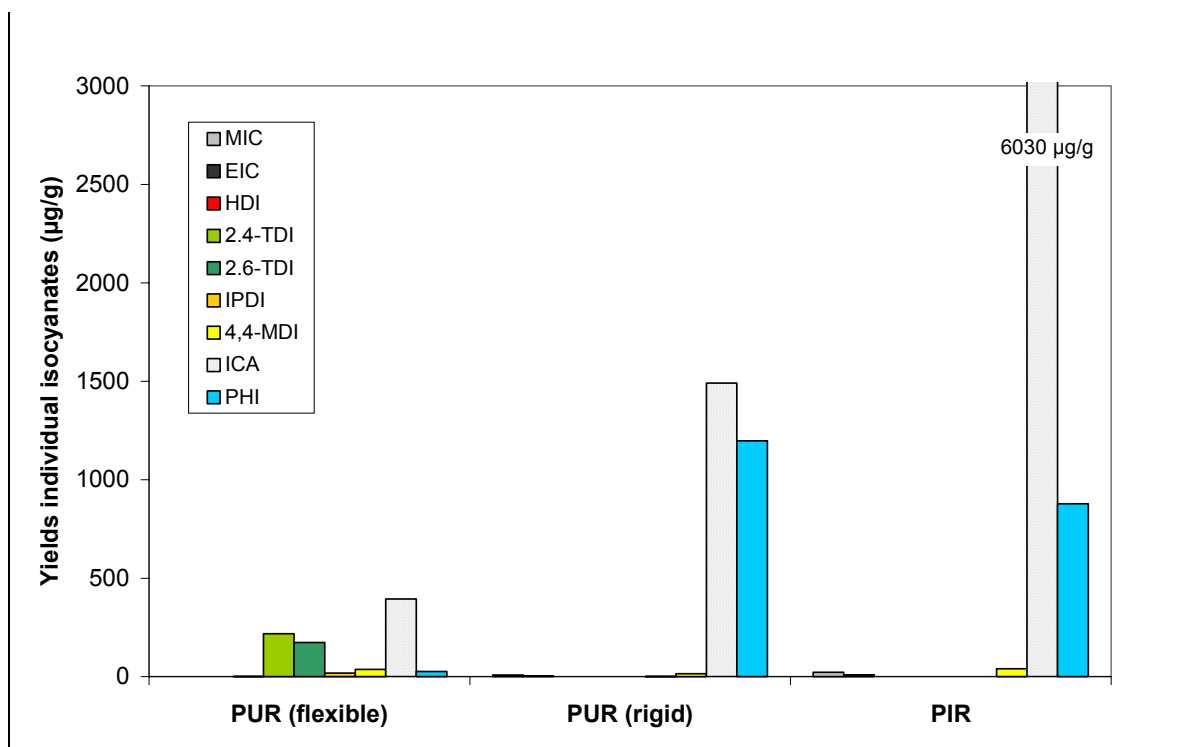


Figure 11 Yields of individual isocyanates from the PUR products.

Amines and/or amine isocyanates were found from all PUR foam materials (see Figure 12). Most significant were the relative amounts found from the flexible PUR foam. Mainly three different species of toluene-aminoisocyanates (TAI) were found; the total

yield was 320 $\mu\text{g/g}$, i.e. approximately 37% compared to the total yield of isocyanates from this material. The highest absolute amounts of amines were, however, found from the rigid PUR foam. A yield of 490 $\mu\text{g/g}$ MDA was found from this material, which is 18% of the total yield of isocyanates.

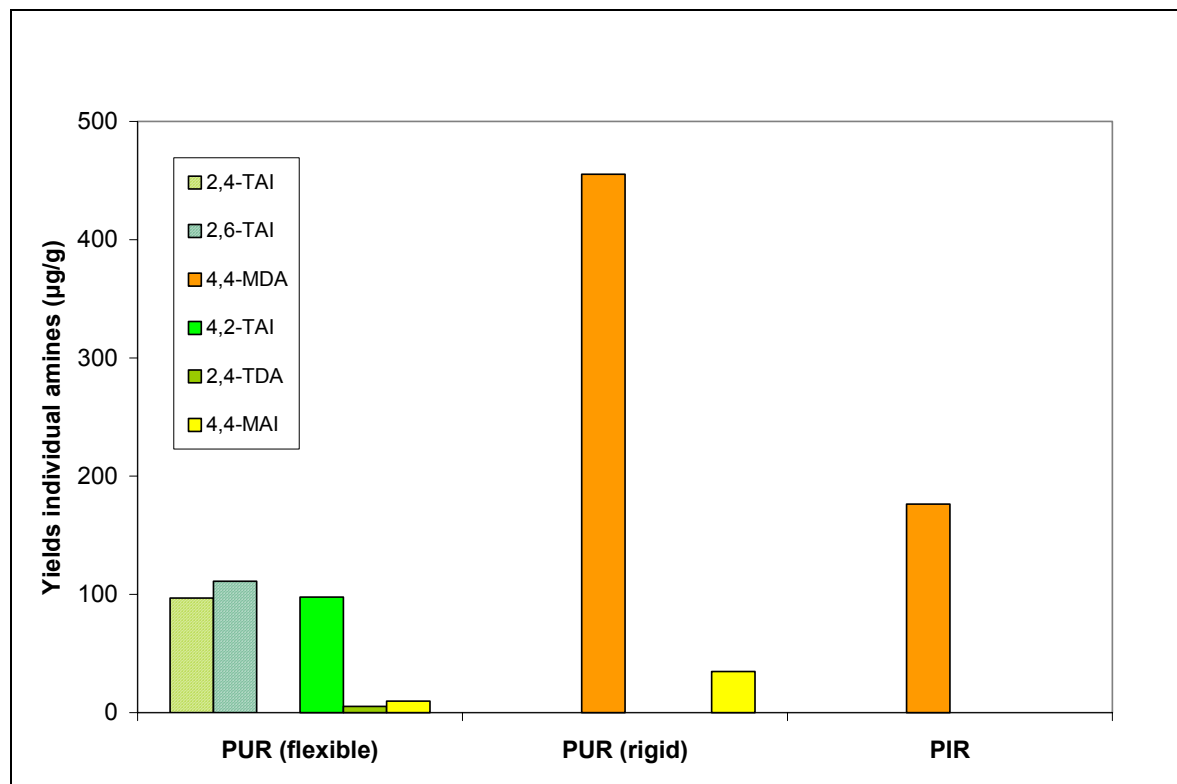


Figure 12 Yields of individual amines from the PUR products.

Three wood-based materials were included in the test series. All of these materials emitted isocyanates during the combustion in the Cone calorimeter. The concentrations found from the Particleboard were much higher compared to the other material, which was expected as Particleboard is made from a nitrogen-containing (urea-based) binder and wood fibres. The dominating isocyanate emitted from the Particleboard was ICA, as was the case for Plywood. For the Wood sample, however, 2,4-TDI and 2,6-TDI were the dominating species produced. The individual isocyanates found from the wood materials are shown in Figure 13.

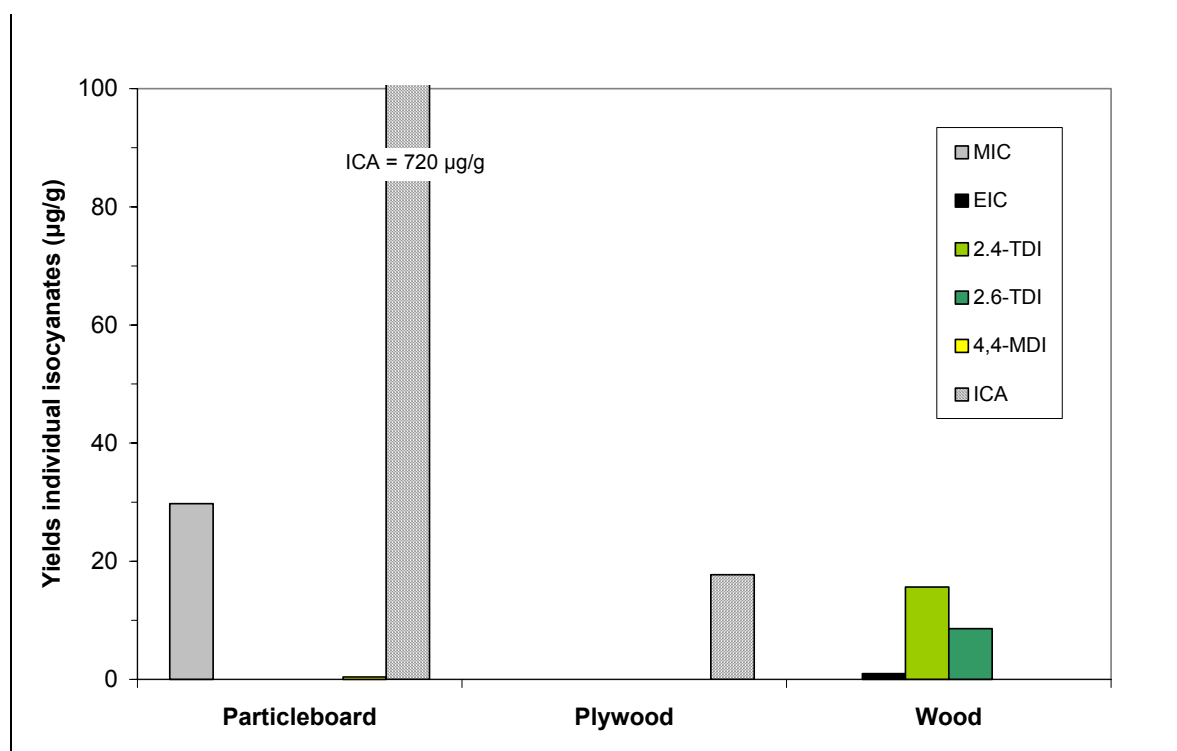


Figure 13 Yields of total isocyanates from the wood products.

Wool as well as Melamine and Nitrile rubber all contain nitrogen in their chemical structure, and would therefore be theoretical potential isocyanate forming during thermal breakdown. The production of isocyanates is, however, not as obvious for these materials as for some of the materials previously discussed (e.g. mineral fibre insulation, PUR, etc.). Considerable amounts of isocyanates were, however, measured from these materials. ICA was produced almost exclusively in all three cases.

There must have been sources of nitrogen also in the samples of Bitumen, FR4-laminate and PVC flooring material, as isocyanates also were found from these materials. The exact composition of these materials is, however, unknown and they could contain nitrogen based additives or contaminants. From the Bitumen and PVC samples only ICA was found, whereas lower amounts of PHI and MIC were found from the FR4-laminate in addition to ICA.

Cables may contain PUR in the form of a lacquer-layer on the copper conductors, or in the form of glue applied in the manufacturing process. The exact composition of the cable products tested here is to a large extent unknown, however, regarding the fluoropolymer cable, information were available that a PUR-glue was included in this cable. As can be seen from Figure 9, traces of isocyanates were found from all cable products. The highest concentrations were measured for the Optical cable. ICA was exclusively found, or dominating, for all Cable products except for the fluoropolymer cable, where ICA and 2,4-TDI were found in equivalent amounts.

In the full-scale room test with the sofa, considerable amounts of isocyanates were produced. The average concentration measured during the whole test period in the smoke gas duct of the room corner was approximately 0.5 ppm ($920 \mu\text{g}/\text{m}^3$). This concentration may seem low; one must, however, consider the fact that the smoke gases coming out of the room are diluted 5-10 times in the duct, and that the peak concentration must have been much higher. Comparing with the IDLH value of 3 ppm, the concentrations of

isocyanates emitted from the sofa must have been a potential health hazard. The isocyanates found from the room experiment were almost exclusively ICA with only low amounts of MIC, PHI and 2,4-TDI. The ratio of ICA to TDI was much higher in this full-scale experiments compared to the combustion of flexible PUR in the Cone calorimeter. Although there is no information available on the exact composition of the two flexible PUR materials in these tests, one could intimate from the results that there was a higher efficiency in breakdown of the TDI-isocyanates from the PUR material to simple ICA in the full-scale test.

Approximately 2.5% of the isocyanates measured in the Room-Corner experiment were found on the particulate phase collected on the Impinger filter^{xiii}. It can be seen from comparison with Table 4 below that this figure is comparable to Melamine and Particleboard. To know if this is to be considered as an enrichment of isocyanates in the particle phase, one would have to know the yield of such particles from the combustion. Unfortunately it is difficult to obtain such information from this experimental set-up. In the small-scale Cone calorimeter, this is more easily done.

A rough estimate of the enrichment of isocyanate on the solid phase can be calculated by comparing the amount of isocyanates collected on the particulate fraction at the impinger flask filter to the amount of isocyanates collected in the impinger liquid phase. This relation is then compared to the quotient between the mass of particles collectable on the impinger flask filter^{xiii} and the rest of the mass loss during the combustion (i.e. gas and particles that are collectable in the impinger flask solution). In mathematical form, this is expressed as:

$$\frac{\text{isocyanates collected on filter}}{\text{isocyanates collected in impinger flask}} = A \quad (1)$$

$$\frac{\text{mass of particles on filter}}{\text{total sample mass loss in test} - \text{mass of particles on filter}} = B^{\text{ xiii}} \quad (2)$$

$$\frac{A}{B} = \text{Enrichment quotient} \quad (3)$$

If the quotient defined by equation (3) is greater than unity, then there is an enrichment of isocyanates on the particulate phase. Note that this calculation is based on the mass of isocyanates and therefore do not consider the possibility of obtaining isocyanates of different molecular types in the different phases. However, the calculation demonstrates that for some materials it is probable that large amounts of isocyanates will be present in the particle phase. It would be very interesting to determine the survivability of these highly reactive compounds on the particulate phase. This would give an indication of health hazards related to the isocyanates generated, far away from the fire.

It is further interesting to note that some materials seem to produce very little isocyanates in the particle phase, e.g. the FR4 material, while others, such as wood, exhibit an enrichment of isocyanates in the particulate phase. Wood is a material that burns very well in a Cone calorimeter test, and it is clear that any isocyanate molecule in the gas phase will be oxidized very efficiently. Wood does not therefore produce very much total isocyanate. It is logical that a molecule on the particulate phase that evidently has not

^{xiii} Particles that are collectable on the impinger filter have particle aerodynamic diameter in the range (0.1 μm , 1.5 μm).

been subjected to a complete oxidation, will stand a greater chance to ‘survive’. This could explain the enrichment of isocyanates on the particulate phase in wood combustion.

Table 4 Data on particles and phase distribution of isocyanates.

| Material | Total mass loss (g) | Yield particulates (mg/g) | Yield impinger filter particulates (mg/g) | Yield total isocyanates (mg/g) | Yield ^{xiii} iso-cyanates on imp. filter particulates (mg/g) | C (see eq. 3) |
|---------------------------|---------------------|---------------------------|---|--------------------------------|---|---------------|
| Glass fibre | 2.29 | 28.1 | 7.4 | 82.1 | 0.857 | 1.43 |
| Mineral fibre | 0.5 | 54.2 | 24.9 | 68.9 | 1.04 | 0.62 |
| Wood | 42.5 | 2.4 | 1.7 | 0.025 | 0.0026 | 67.8 |
| Bitumen | 17.12 | 38.1 | 28.5 | 0.093 | 0.00 | 0.00 |
| Polystyrene | 3.01 | 125.8 | 13.7 | 0.00 | 0.00 | 0.00 |
| Nitrile rubber | 7.67 | 24.6 | 22.1 | 3.68 | 0.0002 | 0.003 |
| PVC | 15.92 | 57.4 | 51.6 | 0.077 | 0.00 | 0.00 |
| Fluoropolymer | 7.41 | 25.4 | 22.9 | 0.00 | 0.00 | 0.00 |
| FR4 laminate | 4.80 | 138.8 | 115.0 | 0.442 | 0.00 | 0.00 |
| Melamine | 8.77 | 18.0 | 9.3 | 1.98 | 0.049 | 2.71 |
| Wool | 3.07 | 21.9 | 16.4 | 1.3 | 0.00 | 0.00 |
| Particle board | 56.5 | 3.9 | 3.4 | 0.749 | 0.018 | 7.28 |
| PUR (flexible) | 6.80 | 26.1 | 3.2 | 0.869* | 0.061 | 23.7 |
| PUR (rigid) | N.M | N.M | N.M | 2.7* | 0.057 | N.M |
| PIR | N.M | N.M | N.M | 7.0* | 0.156 | N.M |
| Plywood | 7.3 | N.M. | N.M. | 0.0177 | N.M. | N.M. |
| Polyethylene pellets | 25.2 | 35.2 | 9.1 | 0.003 | 0.00 | 0.00 |
| Polyethylene cable | 15.9 | 50.6 | 32.1 | 0.0133 | 0.00 | 0.00 |
| PVC+ fluoro-polymer cable | 37.8 | 42.5 | 35.1 | 0.0057 | 0.00 | 0.00 |
| Fluoropolymer cable | 21.3 | 101.7 | 13.5 | 0.0615 | 0.0027 | 3.37 |
| PVC cable | 51.2 | 38.6 | 13.5 | 0.0061 | 0.00 | 0.00 |
| Optical cable | 22.7 | 29.0 | 21.1 | 0.0946 | 0.00 | 0.00 |

* The yield of amine-isocyanates is not included:

PUR (flexible): 0.33 mg/g; PUR (rigid): 0.49 mg/g; PIR: 0.18 mg/g

Figure 14 shows the total isocyanate (*volume*-based) concentration found in the Cone Calorimeter (and Room-Corner test) exhaust duct for all the different materials (with conc.>0) tested in this project (compare the *mass*-based concentrations in Figure 9). As can be seen, the numbers are quite high for some of the materials and the gas should be considered a health hazard based on isocyanate concentration alone, at least for some of the materials tested. A particular characteristic of the isocyanates is their toxicity even at very low levels.

Indeed, it is quite remarkable that the isocyanate concentrations measured are so high since the combustion circumstances in the Cone calorimeter are in favour of total oxidation, due to well-ventilated conditions. This might be observed for other, more well known combustion-generated threats to human health, such as CO and HCN, that are (for

most materials) far from reaching dangerous levels in the calorimeter exhaust duct. This indicates that the capability of materials to generate isocyanates must be taken into consideration when the fire risk analysis is done. To our knowledge, this potential health hazard related to combustion-generated isocyanates has not previously been reported. Table 5 demonstrates the measured toxicity from isocyanates and other toxic compounds for a selected number of materials.

Table 5 'Toxic hazard factors' for isocyanates compared to inorganic gas species for some selected materials (quotient of measured average concentration and NIOSH IDLH-value).

| Material | Isocyanates | Inorganic gases |
|-----------------------------|--------------------|--|
| Glass fibre | 1.42 | HCN = 0.04; NH ₃ = 0.04; CO = 0.01 |
| Nitrile rubber | 0.72 | HCl = 1.19; HCN = 0.12; SO ₂ = 0.11; NH ₃ = 0.06; CO = 0.05 |
| Melamine | 0.62 | HCN = 0.12; SO ₂ = 0.11; CO = 0.08; NO = 0.08; NH ₃ = 0.01 |
| PUR (rigid) | 0.60 | HCN = 0.44; HCl = 0.23; CO = 0.15; NO = 0.14 |
| PIR | 0.56 | HCN = 0.12; HCl = 0.07; CO = 0.05 |
| Particle board | 0.45 | NO = 0.16; CO = 0.02; NH ₃ = 0.02 |
| Wool | 0.19 | SO ₂ = 0.21; NO = 0.10; (HCN < 0.04; CO < 0.01; NH ₃ < 0.01) |
| Mineral fibre | 0.18 | (HCN < 0.04; NH ₃ < 0.01; CO < 0.01) |
| PUR (flexible) | 0.14 | NO = 0.14; HCN = 0.04; CO = 0.02 |
| FR4-laminate | 0.13 | HBr = 1.48; HCl = 0.24; CO = 0.13; HCN = 0.09 |
| Optical cable | 0.085 | HCl = 15.7; HBr = 0.49; CO = 0.13; HCN = 0.09 |
| Bitumen | 0.039 | CO = 0.07* |
| PVC | 0.035 | HCl = 10.3; CO = 0.12 |
| Fluoropolymer-cable | 0.011 | HF = 9.1; CO = 0.08 |
| PVC-cable | 0.0062 | HCl = 11.3; CO = 0.19 |
| Plywood | 0.0056 | CO = 0.06 |
| PVC+fluoropolymer cable | 0.0040 | HF = 10.7; HCl = 7.77; CO = 0.19 |
| Wood | 0.0032 | CO = 0.006* |
| Polyethylene-cable | 0.0032 | CO = 0.03* |
| Polyethylene-pellets | 0.0010 | CO = 0.02 |
| Sofa; full-scale experiment | 0.17 | CO = 0.30* |

* No FTIR data in this test, CO data from NDIR-analyser.

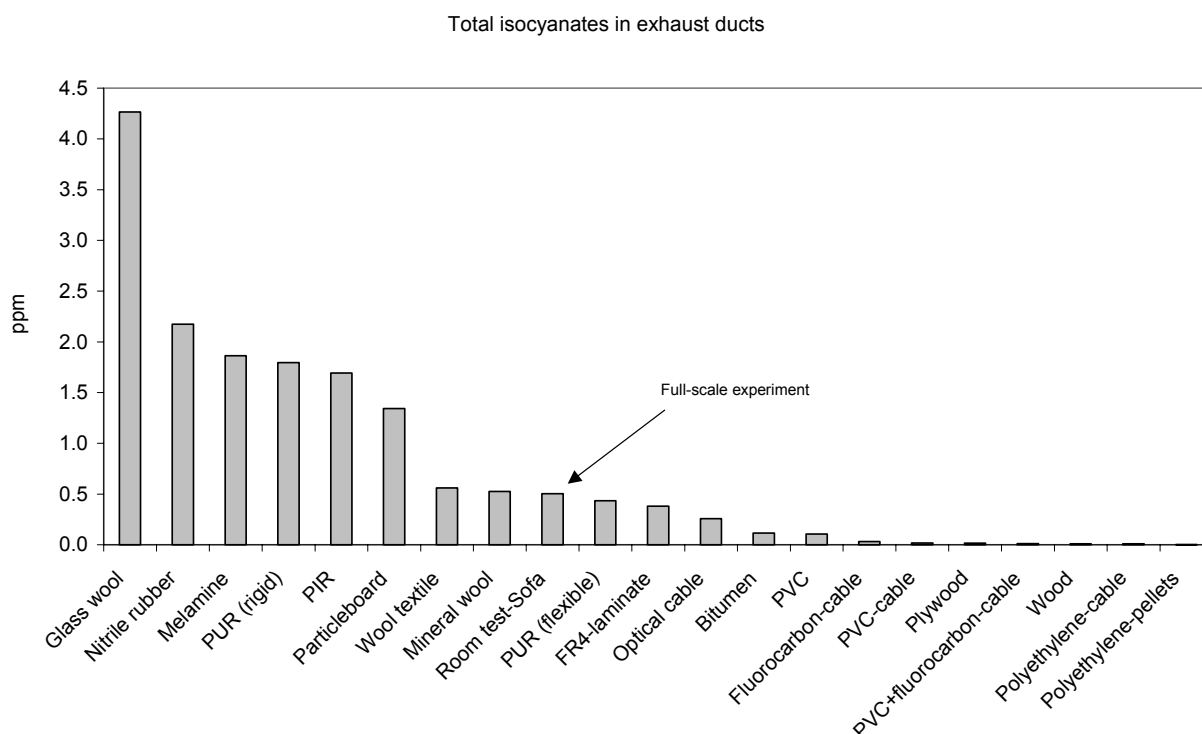


Figure 14 Isocyanate mean concentration in Cone Calorimeter and Room-Corner exhaust duct.

4.3 Investigation of exposure of isocyanates in mattress test

In order to investigate the exposure of people working in the vicinity of fires including PUR material to isocyanates, measurements were conducted in connection with a series of large-scale fire tests. Measurements were conducted both on the air close to the fire test and also on the staff, to determine whether they had increased levels of isocyanate metabolites in their body after the test series. Air sampling was conducted according to what has previously been described for the cone calorimeter tests although no sampling line or probe were used, i.e., the air was sampled directly in two separate impinger set-ups.

The experimental context was a test of sprinklers (water mist) for marine applications. The tests were conducted according to IMO Resolution A.800 (19)²³- appendix 2. In this test procedure mattresses are used as a fire source to produce heat and smoke for sprinkler activation. According to the standard the sprinklers should then manage to control the fire. Measurements of isocyanates were conducted for two test scenarios. For both tests the sampling of isocyanates was conducted at the normal observation position for the staff, and at a height of 1.5 m, equivalent to normal breathing height.

In the first test scenario (test A) the fire source was placed in a smaller (normal sized) cabin connected to the middle of a long corridor. The sampling point for isocyanates was placed 2.5 m from one end of the corridor. The sprinklers were activated one minute after ignition of the mattresses and the fire was extinguished after additionally eight minutes. The cabin and corridor were subsequently vented from smoke gases with a fan, directed

towards the opening of the corridor where the isocyanate samplers were placed. The isocyanate sampling continued for a total of 14 min from the time of ignition.

In the second test scenario (test B) the fire source was placed in a larger (“luxury”) cabin and the sampling point was located 1.5 m from an observatory window, alongside the door opening of the cabin. The sprinklers were activated one minute after ignition and the fire was extinguished after an additional eight minutes. The cabin was vented from smoke gases with a fan after extinction. The isocyanate sampling continued for a total of 16 min from the time of ignition.

The results from the air sampling are given in Table 6.

Table 6 Average concentrations of isocyanates and amines from work-place measurement in mattress tests.

| Fire test | Isocyanates (ppb) | | | | Aminoisocyanates (ppb) | | |
|-----------|-------------------|---------|---------|-----|------------------------|---------|---------|
| | ICA | 2,4-TDI | 2,6-TDI | PHI | 2,4-TAI | 2,6-TAI | 4,2-TAI |
| Test A | 5.5 | 0.8 | 0.3 | - | 0.5 | 0.5 | 1.4 |
| Test B | 44 | 0.3 | 0.9 | 1.1 | - | - | 0.8 |

The total concentration of isocyanates and amines found in Test A was close to 10 ppb, the short-term hygienic limiting value for 5 min exposure. In Test B the concentration was almost 5 times the limiting value. The use of a protective mask would thus be necessary for the staff at all times during this type of fire test. The mattresses contained PUR and the type of individual isocyanates found were those expected from combustion of flexible PUR. ICA was the dominating specie and lower amounts of 2,4-TDI and 2,6-TDI were found. In Test B there seems to have been a better combustion of the PUR material as the ratio of ICA to TDI was much higher in this test. The amines found were various TAI species (amino isocyanate). The finding of a lower relative amount of amines in Test B also correlates with a better combustion in this test.

Two persons from the staff were selected for biological monitoring of isocyanates. One was the test leader who actively participated in all tests, making notes etc. at the observation position during the tests. This person was most exposed to the smoke gases from the tests, thereby representing a high exposure limit. He used a protective mask during much of his work to avoid unnecessary exposure (according to standard safety procedures). The second person spent most of the time away from direct exposure and thus represented in the measurements a low-risk subject.

The biological monitoring of isocyanate exposure were made by analysis of urine from the test persons. Isocyanates are metabolised to amines in the body, which implies that the isocyanate related amine has to be analysed. In this case the exposure of 2,4-TDI, 2,6-TDI, 1,5-NDI and 4,4-MDI were determined through quantification of 2,4-TDA, 2,6-TDA, 1,5-NDA and 4,4-MDA.

Blank tests of urine were taken from both persons before the test series started. No isocyanate related amines were found in these samples. In the samples taken after the test series detectable concentrations were found in the urine from the person with greatest risk for exposure. 2,4-TDA and 2,6-TDA were found, and the measured concentrations were

0.02 µg/mmol respective 0.01 µg/mmol (the concentration unit is related to mmol U-Kreatinin to compensate for varied urine volumes).

The measured concentration levels in the urine cannot be directly related to a risk for negative health effects, but it can be used as an indication of exposure. Thus, even if a protective mask was used most of the time during the tests, an exposure to isocyanates has been shown. One should note, however, that while ICA was the dominating isocyanate in the smoke gases exposure to ICA cannot be detected by the analyses made in this biological monitoring. Thus one can conclude that the results of the biological tests conducted may not show the full exposure.

5 Conclusions

The main purpose of this project has been to shed some light over fire related particle generation and to investigate the distribution of some chemical species in the particulate and the gas phase respectively. Emphasis has been placed on investigating isocyanates produced during the combustion, and their phase distribution, as well as particles produced in the combustion and the particle size distribution. Both these topics, particles and isocyanates, are highly relevant issues with regards to their acute and long-term health implications but also with regards to the environmental impact of fires. In this project, 18 different base or building materials have been tested together with 6 different end 'products' consisting of four types of cables, one piece of upholstered furniture (a sofa) and mattresses. Five different experimental tests based on different standards have been used.

In spite of the importance of the phenomenon, very little research has, to our knowledge, been presented in the literature to describe particles from fires or the ability of different materials to generate particles. Particle content in the atmosphere has been found to correlate statistically with the health status of a population and it has been demonstrated that increased levels of particles leads to increased mortality. This influence on population health has been attributed to respiratory and cardiac diseases caused by the particles. The smaller particles seem to have a higher potential to cause these effects and such small particles are generated mainly in combustion processes. In this project we have shown that the 'yield' of particles generated varies significantly for different materials but that the mass and number size distributions are very similar for all the materials tested. The highest amounts of particles were obtained from materials that did not burn well (e.g. flame retarded materials). Materials that burn well, e.g. wood-based materials, tend to oxidise much of the organic material available and thereby, minimise the amount of particles in the smoke gas.

The maximum in mass distributions was located at ~0.1-0.3 µm and the number distributions had a maximum at the smallest detectable (with the instrument used) particle size, i.e. at ~30 nm. It seems likely that large amounts of even smaller particles would have been found if instruments for measuring such sizes had been used. All particle measurements, small scale (Cone Calorimeter¹¹), intermediate scale (SBI¹³) and full scale (Room Corner¹²) were performed shortly after the particles were generated and the aging/clustering of smaller entities into larger aggregates of particulate material was probably insignificant. The size distributions observed are probably close to what rescue personnel in the vicinity to a fire will be exposed to.

One specific material tested was a *composite* material, made of a carbon fibre re-enforced vinyl ester. Such materials are frequently used for constructing advanced vehicles, airplanes, helicopters, ships, etc, due to important material characteristics such as a high tensile strength/weight quotient. Since fibres are involved in the material, there have been

some discussions regarding the risk for generating asbestos-like particles in the event of a fire. In order to test this two different fire scenarios were used and the content of fibres in the smoke investigated through visual (SEM and optical microscope) inspection of filters from the experimental exhaust ducts. In the well-ventilated fire scenario no fibres were found but a vitiated test scenario produced numerous fibres ranging from ~70 nm to several μm in thickness and from ~5 to ~50 μm in length. This is an important observation since such fibres are both respirable and have a potentially dangerous geometric shape. Only a single vitiated test was performed in this project and further investigation is necessary to examine the fire parameters responsible for fibre generation.

As in the case of particles from fires very little information is available in the literature concerning the emission of isocyanates from fires. The 'fact' that the health hazards from fire smoke is mainly due to its content of carbon monoxide has long been accepted within the fire community. Recently, this scenario has also come to include hydrogen cyanide. The results from this project indicate that it might be possible to find fire scenarios where the greatest danger from the fire-produced gases is actually related to its content of isocyanates. Certainly, the results show that the isocyanate content should be included when estimating the overall health hazard from fire smoke. This can be verified by looking at the results in Table 5.

In the small scale tests performed, the Isocyanates were always at least potentially as dangerous as any other gaseous substance measured. In some cases, e.g. for the glass fibre insulation material, the isocyanates were largely the dominating dangerous species and the mean concentration during the 15 minutes of experimental time was high enough in the exhaust duct ($\sim 4.2 \text{ ppm} = 1.42 \times \text{IDLH-value}^{\text{iii}}$) to be considered a real danger to human health. Especially keeping in mind the fact that this value was obtained in a highly diluted gas flow in the Cone Calorimeter outlet.

The small-scale test is a well-ventilated scenario, which tends to produce very low amounts of CO and HCN. However, in the full-scale test, a single piece of upholstered furniture was burnt in a Room enclosure, which led to flashover, i.e. a situation where combustion is vitiated. Comparing the levels of CO and isocyanates, it can be seen that the CO (on average) attains 30% of the IDLH-value whereas the Isocyanates reach ~17% of the IDLH value during the experimental period. Thus, when estimating the overall toxic effect of such a gas mixture, the isocyanate contribution should be included to give a full picture of the danger. Similarly in this fire test, the measurements were made in the highly diluted gas of the exhaust duct.

A further, large-scale experiment was performed where mattresses were burnt and isocyanates measured in connection to the fire. Two of the technicians involved in performing the experiments were tested to see if isocyanate metabolites could be found in their urine after the test. One of the persons was not working in the actual experimental spaces but stayed in an adjacent control room, whereas the other worked in the burn hall during the experiment. The first person did not show any metabolites. The officer in the burn hall showed small concentrations of isocyanate metabolites despite of the fact that he used protective gear, including pressurised mask, at all times. The metabolite levels were low but the main isocyanate specie measured in the enclosure during the experiment, ICA, is not traceable through metabolites in the urine, which indicates that the urine sample results may not provide full information concerning the exposure.

6 Future work

It was demonstrated in this project that large amounts of respirable particles are found in smoke close to a fire but also that there were large differences between materials. There is a need to investigate how the particles behave on a longer term, i.e. to study ageing of the particles. It is highly probable that the aging will differ greatly depending on the amount of particles and on the type of substances found in the particles. It is important to understand ageing in order to predict particle behaviour and toxicity in the environment of a fire.

The circumstances for generating the specific, asbestos-like particles obtained from the composite material, also needs further investigation.

It has been shown in this work that isocyanates can be found on fire generated respirable particles. Further work is needed to investigate their transport mechanism into the lungs and the health related effect from such exposure. In this study only well-ventilated combustion conditions was studied with a screening approach for a large number of materials. There is a need to more systematically study the influence of the combustion conditions on the production of isocyanates, e.g. pyrolysis conditions, vitiated conditions etc. Other subjects that require additional research are the reactivity (break-down) of isocyanate compounds when transported away from the fire, and the development a suitable in situ measurement method for isocyanates, suitable for e.g. firemen at a fire scene.

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Appendix

Detailed mass and number size distributions

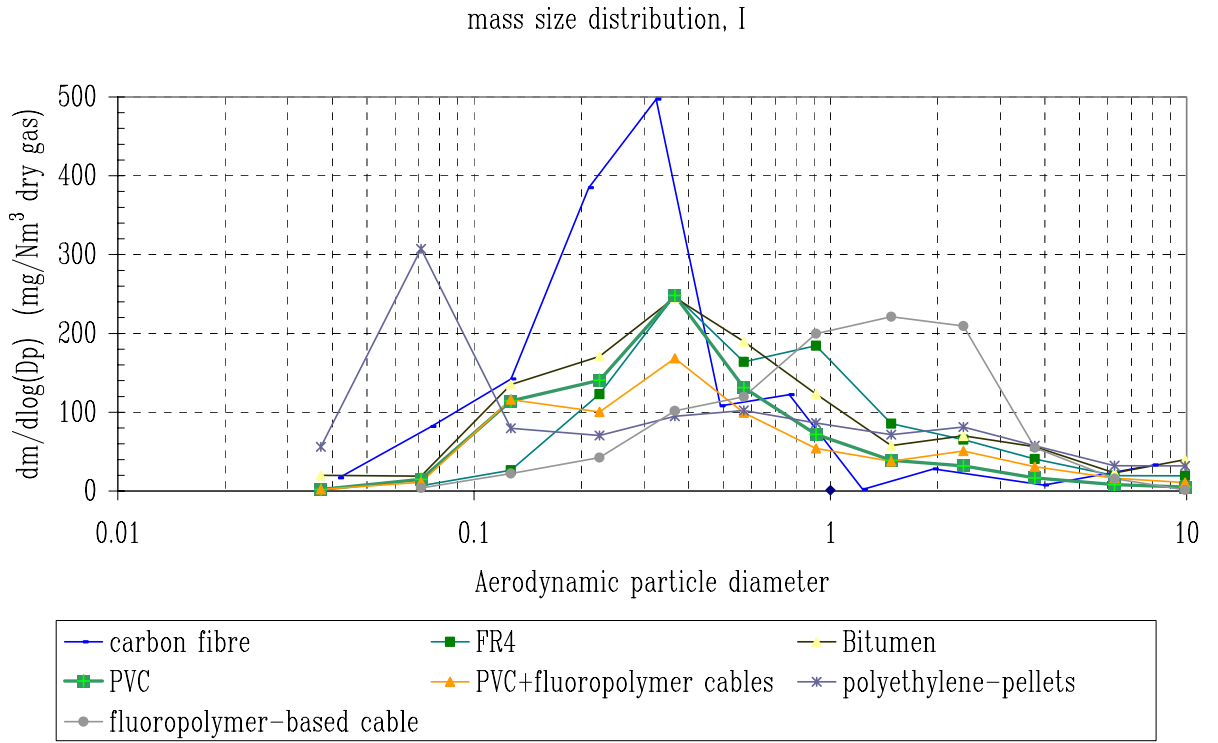


Figure 15 Mass size distribution; non-logarithmic y-axis

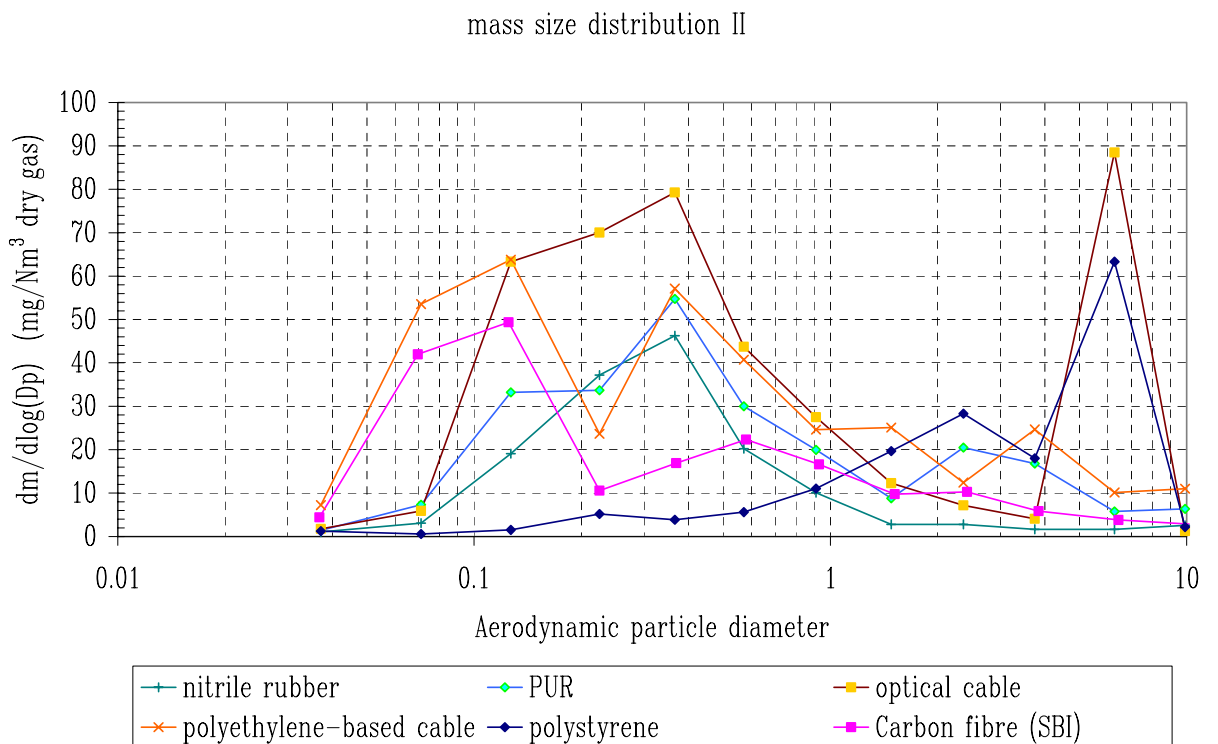


Figure 16 Mass size distribution; non-logarithmic y-axis

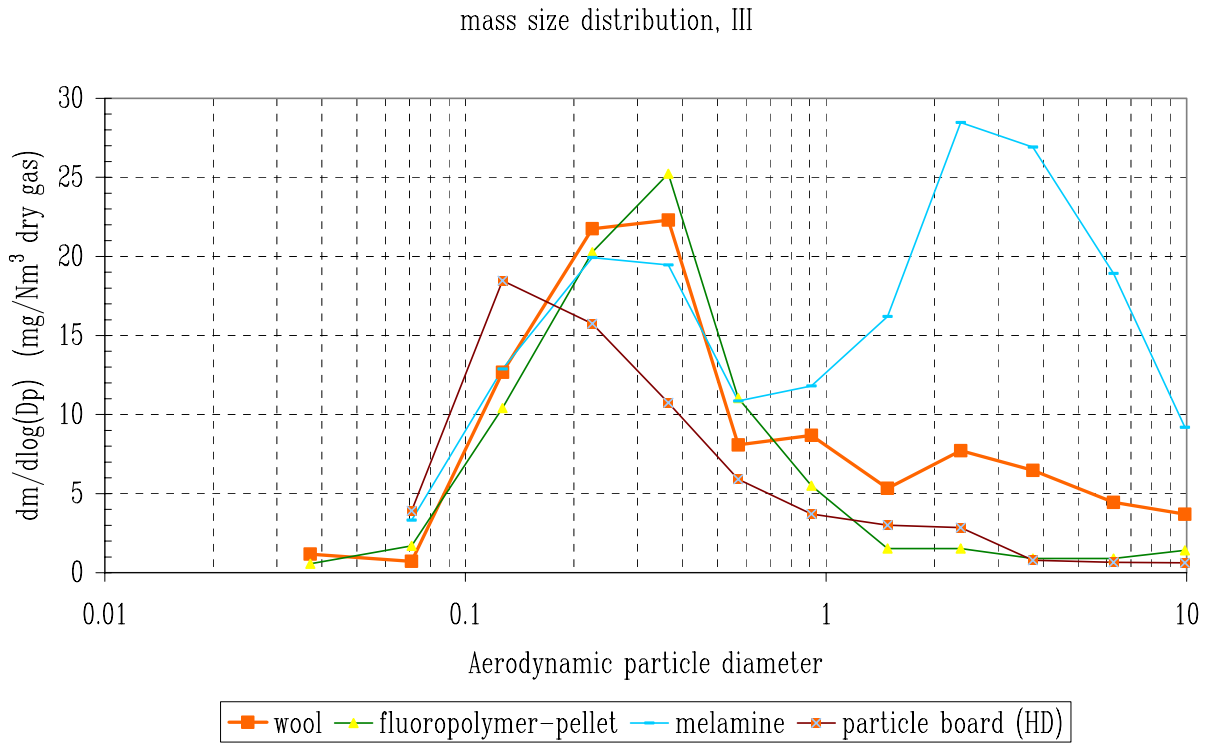


Figure 17 Mass size distribution; non-logarithmic y-axis

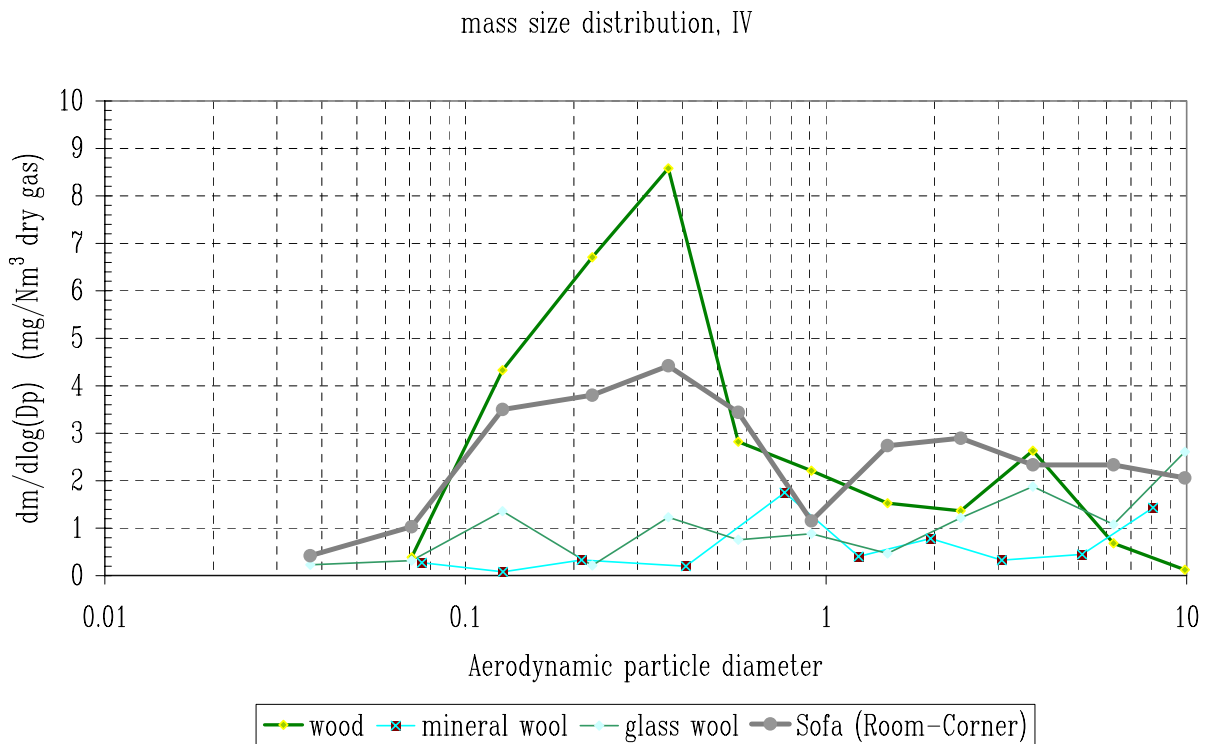


Figure 18 Mass size distribution; non-logarithmic y-axis

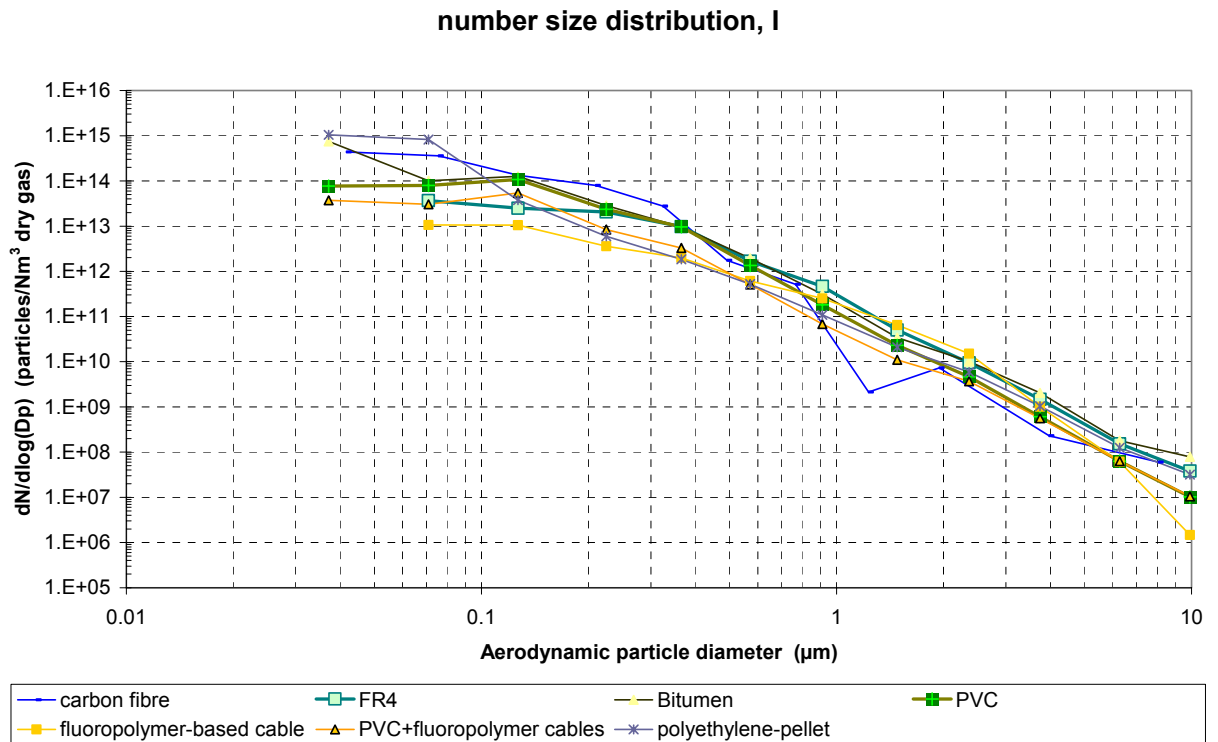


Figure 19 Number size distribution for mass distribution shown in Figure 15

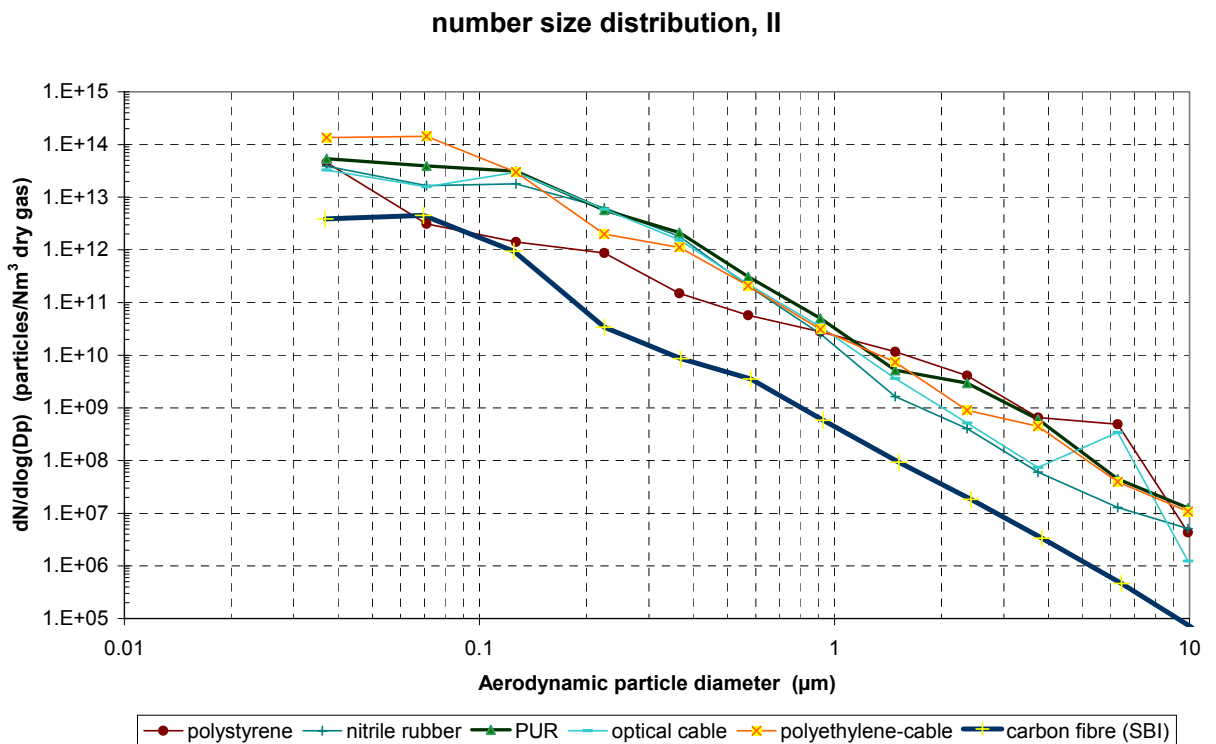


Figure 20 Number size distribution for mass distribution shown in Figure 16

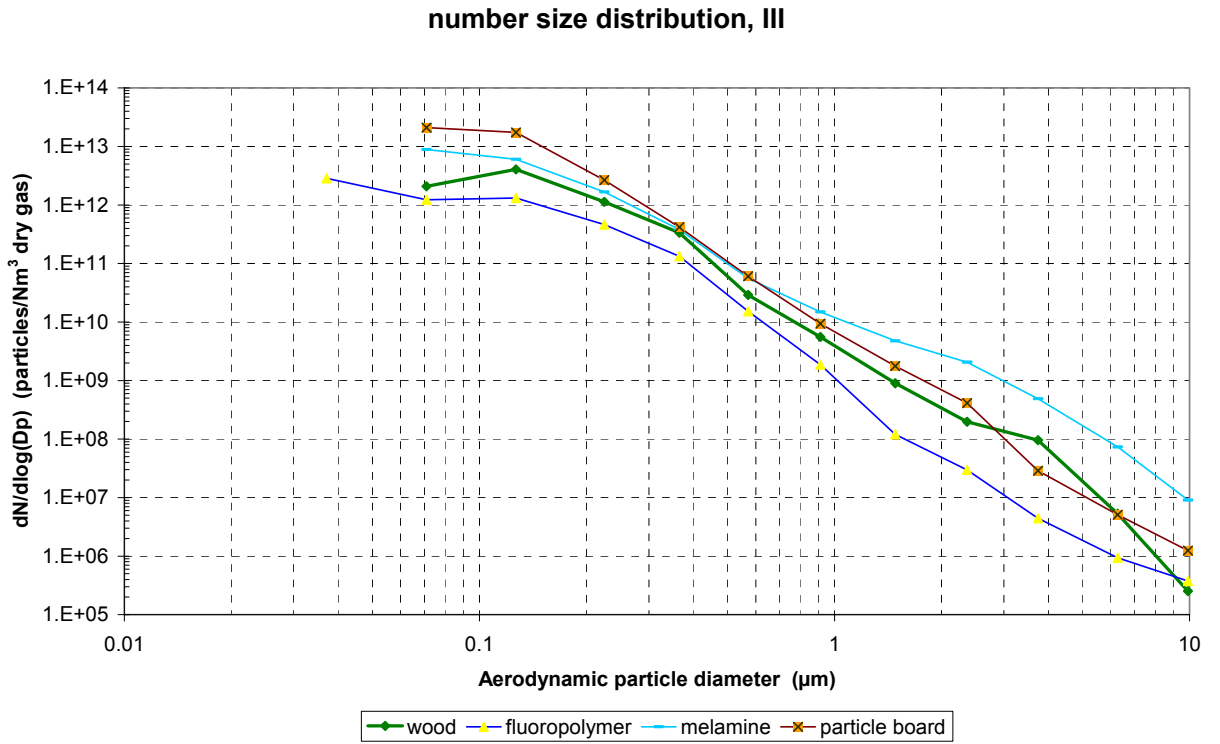


Figure 21 Number size distribution for mass distribution shown in Figure 17

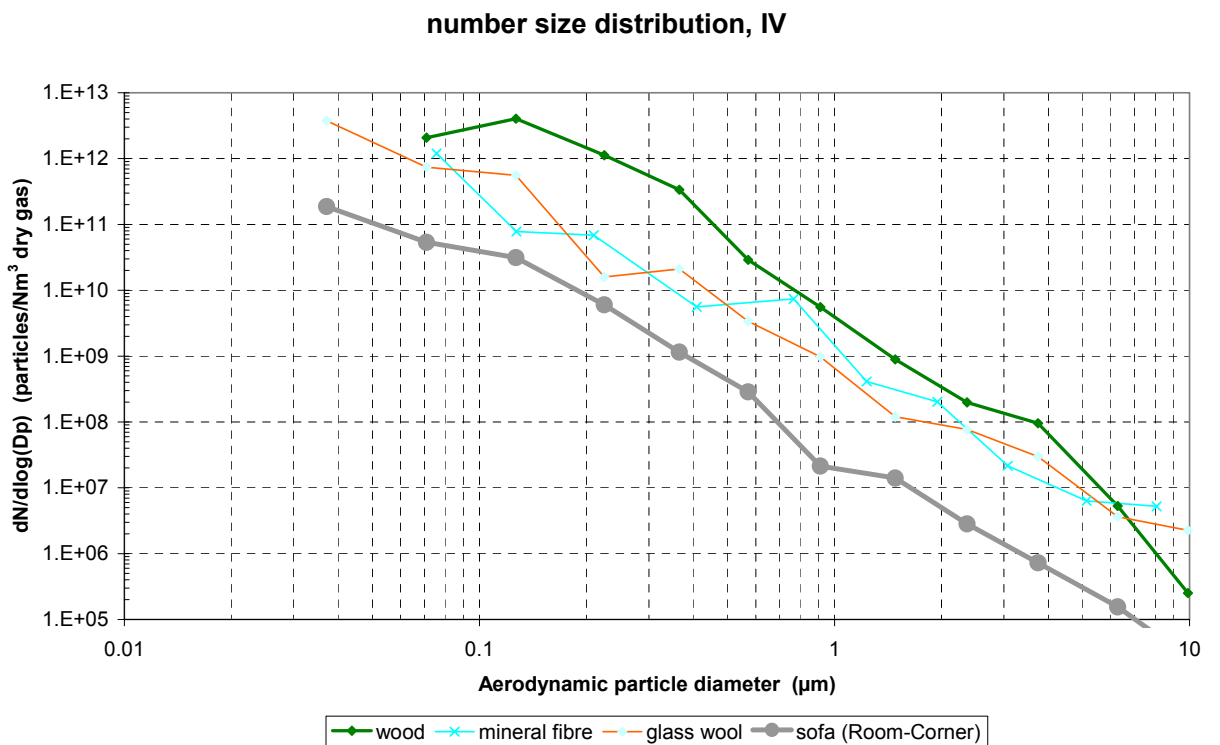


Figure 22 Number size distribution for mass distribution shown in Figure 18

Detailed isocyanate data

For explanation of species abbreviation, see Table 2.

Table 7 Mass concentrations of Isocyanates in Cone calorimeter exhaust, $\mu\text{g}/\text{Nm}^3$.

| Substance | Total conc. | MIC | EIC | PIC | PhI | HDI | 2.4-TDI | 2.6-TDI | IPDI | MDI | ICA |
|--------------------------|-------------|--------|-----|-----|--------|-----|---------|---------|------|-------|--------|
| Glass wool 1 | 8587.2 | 1350.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.6 | 7236.6 |
| Glass wool 2 | 7432.2 | 1289.3 | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 6141.9 |
| Glass wool, average | 8009.7 | 1319.7 | 0.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 | 6689.2 |
| Mineral wool 1 | 1064.6 | 84.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 980.6 |
| Mineral wool 2 | 875.3 | 115.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 759.7 |
| Mineral wool, average | 970.0 | 99.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 870.1 |
| wood | 66.1 | 0.0 | 2.6 | 0.0 | 0.0 | 0.0 | 41.0 | 22.6 | 0.0 | 0.0 | 0.0 |
| Bitumen | 209.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 209.3 |
| Polystyrene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Nitrile rubber | 3920.8 | 14.4 | 0.0 | 0.0 | 5.1 | 0.0 | 0.0 | 0.0 | 0.0 | 1.4 | 3900.0 |
| PVC | 190.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 190.0 |
| FR4 | 759.8 | 17.3 | 0.0 | 0.0 | 107.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 635.0 |
| Melamine | 3359.6 | 24.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3335.6 |
| Fluoropolymer | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Wool 1 | 655.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 655.0 |
| Wool 2 | 1372.3 | 8.4 | 9.1 | 4.2 | 2.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1348.6 |
| Wool, average | 1013.6 | 4.2 | 4.5 | 2.1 | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1001.8 |
| Particle board 1 | 2697.0 | 110.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2587.0 |
| Particle board 2 | 2557.7 | 96.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 4.0 | 2457.3 |
| Particle board 3 | 2073.3 | 85.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1988.0 |
| Particle board average | 2442.7 | 97.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.3 | 2344.1 |
| PUR flexible 1 | 692.4 | 0.0 | 0.0 | 0.0 | 11.4 | 0.0 | 101.6 | 39.9 | 0.0 | 0.0 | 539.5 |
| PUR flexible 2 | 1400.3 | 0.0 | 0.0 | 0.0 | 60.0 | 0.0 | 391.7 | 293.3 | 0.0 | 0.0 | 655.4 |
| PUR flexible 3 | 1882.5 | 0.0 | 0.0 | 0.0 | 49.5 | 4.9 | 504.5 | 458.7 | 85.0 | 170.0 | 609.9 |
| PUR average (flexible) | 1325.1 | 0.0 | 0.0 | 0.0 | 40.3 | 1.6 | 332.6 | 264.0 | 28.3 | 56.7 | 601.6 |
| PUR (rigid) | 4519.8 | 14.5 | 5.4 | 0.0 | 1993.0 | 0.0 | 0.0 | 0.0 | 0.9 | 24.5 | 2481.5 |
| PIR | 3336.0 | 10.5 | 4.4 | 0.0 | 419.8 | 0.0 | 0.0 | 0.0 | 0.0 | 18.9 | 2882.4 |
| Plywood | 30.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 30.4 |
| Polyethylene-pellets | 5.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 5.5 |
| Polyethylene-cable | 17.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 17.1 |
| PVC+ Fluoropolymer cable | 22.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.9 | 0.0 | 0.0 | 0.0 | 21.2 |
| Fluoropolymer-cable | 99.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 46.5 | 0.0 | 0.0 | 5.8 | 46.8 |
| PVC-cable | 33.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 33.5 |
| Optical cable | 463.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.9 | 0.0 | 0.0 | 0.0 | 460.0 |

Table 8 Volume concentration of Isocyanates in Cone calorimeter exhaust, ppb.

| Substance | Total conc. | MIC | EIC | PIC | PhI | HDI | 2.4-TDI | 2.6-TDI | IPDI | MDI | ICA |
|--------------|-------------|-------|-----|-----|-----|-----|---------|---------|------|-----|--------|
| Glass wool 1 | 4582.5 | 562.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 4019.9 |

| | | | | | | | | | | | |
|--------------------------|--------|-------|-----|-----|-------|-----|------|------|-----|------|--------|
| Glass wool 2 | 3949.4 | 537.2 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3411.8 |
| Glass wool, average | 4265.9 | 549.9 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3715.9 |
| Mineral wool 1 | 579.7 | 35.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 544.7 |
| Mineral wool 2 | 470.2 | 48.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 422.0 |
| Mineral wool, average | 525.0 | 41.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 483.4 |
| wood | 9.7 | 0.0 | 0.9 | 0.0 | 0.0 | 0.0 | 5.7 | 3.1 | 0.0 | 0.0 | 0.0 |
| Bitumen | 116.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 116.2 |
| Polystyrene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Nitrile rubber | 2173.6 | 6.0 | 0.0 | 0.0 | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 2166.5 |
| PVC | 105.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 105.5 |
| FR4 | 381.9 | 7.2 | 0.0 | 0.0 | 21.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 352.7 |
| Melamine | 1863.0 | 10.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1852.9 |
| Fluoropolymer | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Wool 1 | 363.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 363.9 |
| Wool 2 | 757.3 | 3.5 | 3.0 | 1.2 | 0.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 749.1 |
| Wool, average | 560.6 | 1.7 | 1.5 | 0.6 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 556.5 |
| Particle board 1 | 1482.9 | 45.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1437.1 |
| Particle board 2 | 1405.6 | 40.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.4 | 1365.0 |
| Particle board 3 | 1139.9 | 35.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1104.4 |
| Particle board average | 1342.8 | 40.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 1302.2 |
| PUR flexible 1 | 321.7 | 0.0 | 0.0 | 0.0 | 2.3 | 0.0 | 14.1 | 5.5 | 0.0 | 0.0 | 299.7 |
| PUR flexible 2 | 471.4 | 0.0 | 0.0 | 0.0 | 12.2 | 0.0 | 54.4 | 40.7 | 0.0 | 0.0 | 364.1 |
| PUR flexible 3 | 509.0 | 0.0 | 0.0 | 0.0 | 10.1 | 0.7 | 70.1 | 63.7 | 9.2 | 16.3 | 338.8 |
| PUR average (flexible) | 434.0 | 0.0 | 0.0 | 0.0 | 8.2 | 0.2 | 46.2 | 36.7 | 3.1 | 5.4 | 334.2 |
| PUR (rigid) | 1795.5 | 6.0 | 1.8 | 0.0 | 406.7 | 0.0 | 0.0 | 0.0 | 0.1 | 2.4 | 1378.5 |
| PIR | 1694.5 | 4.4 | 1.5 | 0.0 | 85.7 | 0.0 | 0.0 | 0.0 | 0.0 | 1.8 | 1601.2 |
| Plywood | 16.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 16.9 |
| Polyethylene-pellets | 3.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.0 |
| Polyethylene-cable | 9.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 9.5 |
| PVC+ fluoropolymer cable | 11.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 11.8 |
| Fluoropolymer-cable | 33.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 6.5 | 0.0 | 0.0 | 0.6 | 26.0 |
| PVC-cable | 18.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 18.6 |
| Optical cable | 256.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.5 | 0.0 | 0.0 | 0.0 | 255.5 |

Table 9 Yield of Isocyanates in Cone calorimeter experiments, $\mu\text{g/g}$.

| Substance | Total yield | MIC | EIC | PIC | PhI | HDI | 2.4-TDI | 2.6-TDI | IPDI | MDI | ICA |
|-----------------------|-------------|---------|------|-----|-----|-----|---------|---------|------|-----|---------|
| Glass wool 1 | 77675 | 12211 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 5.7 | 65458.3 |
| Glass wool 2 | 86563.1 | 15016.6 | 11.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 71534.8 |
| Glass wool, average | 82119.3 | 13614.0 | 5.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.9 | 68496.6 |
| Mineral wool 1 | 42159.5 | 3325.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 38833.6 |
| Mineral wool 2 | 34662.5 | 4580.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 30082.2 |
| Mineral wool, average | 38411.0 | 3953.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 34457.9 |
| wood | 25.2 | 0.0 | 1.0 | 0.0 | 0.0 | 0.0 | 15.6 | 8.6 | 0.0 | 0.0 | 0.0 |
| Bitumen | 93.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 93.0 |
| Polystyrene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Nitrile rubber | 3677.5 | 13.5 | 0.0 | 0.0 | 4.7 | 0.0 | 0.0 | 0.0 | 0.0 | 1.3 | 3658.0 |

| | | | | | | | | | | |
|---------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Bitumen | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| FR4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| PVC | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Fluoropolymer | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Polyethylene pellets | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Polyethylene cable | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| PVC+ fluoro-polymer cable | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Fluoropolymer -cable | 9.9 | 5.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 5.0 |
| PVC-cable | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Optical cable | 5.2 | 0.0 | 0.0 | 0.0 | 0.0 | 5.2 | 0.0 | 0.0 | 0.0 | 0.0 |

FTIR data

Table 12 Detailed FTIR data from time period of isocyanate sampling. From top to bottom in each column: average concentration, max concentration, yield of species (- not detected). Note: ambient CO₂ is not subtracted in the table.

| Sample | CO ₂ | CO | HCN | HCl | HF | HBr | SO ₂ | NH ₃ | NO |
|-----------------------|--|------------------------------------|------------------------------------|---------------------------------|----|--------------------------------|-------------------------------------|-------------------------------------|------------------------------------|
| Glass wool 2 | <0.05 % | 14 ppm 46 ppm 0.19 g/g | 2 ppm 7 ppm 0.026 g/g | - | - | - | - | 11 ppm 43 ppm 0.093 g/g | - |
| Mineral wool 2 | <0.05 % | <10 ppm | <2 ppm | - | - | - | - | <2 ppm | - |
| Nitrile rubber | 0,1 % 0.18 % 1.7 g/g | 63 ppm 95 ppm 0.067 g/g | 6 ppm 11 ppm 0.006 g/g | 59 ppm 130 ppm 0.082 g/g | - | - | 10 ppm 21 ppm 0.023 g/g | 17 ppm 35 ppm 0.011 g/g | - |
| PVC | 0.18 % 0.39 % 1.4 g/g | 140 ppm 480 ppm 0.069 g/g | - | 510 ppm 2300 ppm 0.32 g/g | - | - | - | - | - |
| FR4 | 0.09 % 0.26 % 1.0 g/g | 160 ppm 740 ppm 0.11 g/g | 5 ppm 22 ppm 0.0030 g/g | 12 ppm 55 ppm 0.011 g/g | - | 44 ppm 240 ppm 0.088 g/g | - | - | - |
| Melamine | 0.17 % 0.58 % 2.0 g/g | 101 ppm 184 ppm 0.074 g/g | 6 ppm 15 ppm 0.0042 g/g | - | - | - | 11 ppm 22 ppm 0.012 g/g | 4 ppm 24 ppm 0.0016 g/g | 8 ppm 42 ppm 0.0061 g/g |
| Fluoro-polymer Wool 1 | <0.05 % 0.12 % 0.47 % 2.9 g/g | - 11 ppm 23 ppm 0.017 g/g | - <2 ppm 4 ppm 0.0020 g/g | - | -* | - | - 19 ppm 120 ppm 0.065 g/g | - <2 ppm 12 ppm 0.0012 g/g | - 10 ppm 59 ppm 0.016 g/g |
| Wool 2** | 0.14 % 0.53 % 1.3 g/g | 8 ppm 26 ppm 0.0047 g/g | <2 ppm 5 ppm <0.001 g/g | - | - | - | 23 ppm 155 ppm 0.029 g/g | 7 ppm 69 ppm 0.0024 g/g | 11 ppm 61 ppm 0.0064 g/g |
| Particle board 1 | 0.29 % 0.53 % 1.4 g/g | <10 ppm 35 ppm 0.0020 g/g | - | - | - | - | - | 4 ppm 72 ppm <0.001 g/g | 19 ppm 31 ppm 0.0061 g/g |
| Particle board 2 | 0.27 % 0.61 % 1.5 g/g | 28 ppm 110 ppm 0.010 g/g | - | - | - | - | - | 6 ppm 76 ppm 0.0014 g/g | 14 ppm 30 ppm 0.0052 g/g |
| Particle board 3 | 0.26 % 0.59 % 1.5 g/g | 27 ppm 114 ppm 0.010 g/g | - | - | - | - | - | 6 ppm 80 ppm 0.0013 g/g | 15 ppm 30 ppm 0.0059 g/g |
| PUR flexible 1 | 0.22 % 0.89 % 2.4 g/g | 18 ppm 102 ppm 0.013 g/g | 2 ppm 14 ppm 0.0015 g/g | - | - | - | - | - | 14 ppm 66 ppm 0.010 g/g |
| PUR flexible 2 | 0.22 % 0.88 % 2.6 g/g | 18 ppm 98 ppm 0.013 g/g | 2 ppm 15 ppm 0.0014 g/g | - | - | - | - | - | 15 ppm 72 ppm 0.012 g/g |
| PUR flexible 3 | 0.22 % 0.86 % 2.3 g/g | 21 ppm 95 ppm 0.015 g/g | 2 ppm 14 ppm 0.0015 g/g | - | - | - | - | - | 15 ppm 68 ppm 0.011 g/g |
| PUR (rigid) | 0.15 % 0.41 % 1.6 g/g | 175 ppm 710 ppm 0.12 g/g | 22 ppm 98 ppm 0.014 g/g | 11 ppm 51 ppm 0.010 g/g | - | - | - | - | 14 ppm 42 ppm 0.010 g/g |
| PIR | 0.09 % 0.28 % | 63 ppm 104 ppm | 6 ppm 13 ppm | < 5 ppm 29 ppm | - | - | - | - | - |

| | | | | | | | | | |
|---------------------------|----------|------------|-----------|-----------|----------|-----------|---|---|---|
| Plywood | 3.3 g/g | 0.15 g/g | 0.014 g/g | 0.011 g/g | | | | | |
| | 0.19 % | 74 ppm | - | - | - | - | - | - | - |
| | 1.0 % | 130 ppm | | | | | | | |
| Polyethylene-pellets | 2.0 g/g | 0.050 g/g | | | | | | | |
| | 0.30 % | 19 ppm | - | - | - | - | - | - | - |
| | 0.43 % | 35 ppm | | | | | | | |
| Polyethylene-cable*** | 0.53 g/g | 0.0020 g/g | | | | | | | |
| | - | - | - | - | - | - | - | - | - |
| | >0.55 % | > 75 ppm | | | | | | | |
| PVC+ fluoro-polymer cable | 0.17 % | 230 ppm | - | 390 ppm | 320 ppm | - | - | - | - |
| | 0.29 % | 490 ppm | | 990 ppm | 590 ppm | | | | |
| | 1.3 g/g | 0.11 g/g | | 0.16 g/g | 0.10 g/g | | | | |
| fluoro-polymer cable | 0.05 % | 97 ppm | - | - | 270 ppm | - | - | - | - |
| | 0.06 % | 193 ppm | | | 1090 ppm | | | | |
| | - | 0.069 g/g | | | 0.14 g/g | | | | |
| PVC-cable | 0.19 % | 230 ppm | - | 560 ppm | - | - | - | - | - |
| | 0.30 % | 440 ppm | | 1010 ppm | | | | | |
| | 0.58 g/g | 0.044 g/g | | 0.14 g/g | | | | | |
| Optical cable | 0.12 % | 155 ppm | 4 ppm | 780 ppm | - | 15 ppm | - | - | - |
| | 0.19 % | 310 ppm | 7 ppm | 1180 ppm | | 33 ppm | | | |
| | 0.46 g/g | 0.038 g/g | 0.001 g/g | 0.25 g/g | | 0.010 g/g | | | |

* HF was not detected in this test were the material was pyrolysing only.

** Two layers of sample were used in test Wool 2 whereas one layer was used in test Wool 1.

*** No data in first part of test due to mistake in sampling.