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Combustion Products from Fires

Influence from ventilation conditions

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Abstract
The production of combustion products is discussed, especially with respect to the influence of ventilation conditions. Results are presented and compared, from different experimental set-ups. Experimental techniques are presented and discussed.

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Table of contents

PAPER I

PAPER II

PAPER III

List of papers

Papers included in this dissertation

Paper I
"Determination of the Equivalence Ratio during Fire, Comparison of Techniques"
Berit Andersson, Göran Holmstedt and Anders Dagneryd
Presented at the Seventh IAFSS symposium in Worcester, USA, June 16-21, 2002, pp 295-308.

Paper II
"Simulated Fires in Substances of Pesticide Type"
Berit Andersson, Vytenis Babrauskas, Göran Holmstedt, Stefan Särdqvist and Göran Winter
Department of Fire Safety Engineering, Lund University, Report 3087, 1996

Paper III
"Combustion Products Generated by Hetero-organic Fuels on Four Different Fire Test Scales"
Berit Andersson, Frank Markert and Göran Holmstedt
Submitted to the Fire Safety Journal, 2003-06-04.

Other related publications, not included in this dissertation

"Production of Toxic Gases – Scaling Effects"
Andersson B., Holmstedt G. and Särdqvist S.
Presented at the STEP Meeting in Cadarache, France, May 16-18, 1994.

"Combustion of Chemical Substances and the Impact on the Environment of the Fire Products – 1/3 Scale Room Furnace Experiments"
Andersson B., Davie F., Holmstedt G., Kenéz A. and Särdqvist S.
Department of Fire Safety Engineering, Lund University, Report 3074, 1994.

"Simulated Fires in Substances of Pesticide Type"
Andersson B., Holmstedt G, Särdqvist S. and Winter G.
Industrial Fires III Workshop – Proceedings, Risø, Denmark, Sept. 17-18, 1996, pp 17-27.

"Scaling of Combustion Products: Initial Results from the TOXFIRE Study"
Andersson B., Babrauskas V., Holmstedt G., Särdqvist S. and Winter G.
Industrial Fires III Workshop – Proceedings, Risø, Denmark, September 17-18, 1996, pp 65-74.

"Scaling of Combustion Products from Chemical Warehouse Fires"
Andersson B., Babrauskas V., Holmstedt G., Särdqvist S. and Winter G.
Poster presented at the Fifth IAFSS Symposium, Melbourne, Australia, March 3-7, 1998, p 1351.

"Simulated Fires in Substances of Pesticide Type"
Andersson B., Babrauskas V., Holmstedt G., Särdqvist S. and Winter G.
Poster presented at the Fifth IAFSS Symposium, Melbourne, Australia, March 3-7, 1998, p 1352.

"Scaling Experiments to Assess Chemical Warehouse Fires"
Markert, F., Andersson, B. and Holmstedt G.
Published at the SAFETYNET, Internet seminar, 1999.

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To my family: Thorbjörn, Katrin and Patrik, you deserve special thanks for your continuous support and for always being there for me.

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Lund September 2003
Berit

1 Introduction

Fire can be described as an exothermic oxidative process or as undesirable and hazardous combustion. Regardless of the description, combustion products are evolved during fire. These combustion products can cause a great deal of damage to property and the environment, and cause death or injury to people. The damage can also give rise to much human suffering and considerable economic loss. In Sweden, the number of deaths caused by fire is just over 100 every year, and about 800 people require medical care due to fire-related injuries. The economic losses due to fire are of the order of SEK 5000 million per year.

Fire tests and experiments are performed in order to investigate the behaviour of materials, products and construction elements when exposed to fire. Tests can be designed to examine different characteristics such as ignitability, temperature development, radiation, charring properties, and the production of smoke and combustion gases. In this licentiate dissertation a number of different types of experiments in which smoke and combustion gases were measured, are presented and discussed. The influence of temperature, oxygen concentration and rate of heat release on the composition of the combustion gases is also discussed.

The results from fire tests and experiments can be used, for example as input in fire hazard assessments, in risk analysis and in operational planning carried out by the fire brigade. Information is of course sought from fires that have occurred, but information on specific combustion products, or materials or products burned, is rarely found. It is therefore necessary to perform fire tests and experiments in order to collect basic data as input in fire hazard analysis or risk assessment.

1.1 Background and objectives

Fires in warehouses where chemicals are stored can constitute a serious threat to people and to the environment through the spread of toxic compounds with the fire gases. Toxic components may consist of combustion products or the compounds themselves stored in the warehouse. Particles may also be distributed over large areas together with the fire gases. These particles may consist of soot, unburned materials and organic and inorganic substances collected on the soot particles. Water is often used for the suppression of warehouse fires and the contaminated extinguishing water can also cause damage to the environment.

One of the most well-known warehouse fires involving chemicals is the fire at the Sandoz industrial area near Basel, Switzerland on November 1, 1986. The fire took place in a warehouse where 1.25 million kg chemicals and packaging materials were stored. The chemicals were mainly pesticides, herbicides and highly flammable liquids. The fire caused considerable discomfort to people in the surrounding areas and severe damage to the environment, mainly to the river Rhine, where contaminated water from the fire-fighting operations and residual chemicals from the warehouse collected. A large number of fish died and other damage to the fauna was also noticed. The fire plume contained sulphur and other organic and inorganic substances, which spread over the Basel area, causing anxiety and discomfort among the inhabitants.

The work on combustion gases produced in fire experiments presented in this dissertation was initiated in 1991, when the first project in this area was started as part of the CEC STEP Programme. The project had the title: *Combustion of chemical substances and the impact on the environment of the fire products*. The main objective of this project was to obtain data concerning the identification of combustion products from fires in warehouses containing commercial chemicals. A summary of the outcome of the project can be found in the final report by L. Smith-Hansen [1].

The STEP project was followed by another CEC project in the Environment Programme. This new project, which started in 1993, had the title: *Guidelines for management of fires in chemical warehouses*. The project was named TOXFIRE, which is the acronym that will be used here. The project was carried out by an international consortium including the following partners:

- The Risø National Laboratory, Denmark, co-ordinator
- The Danish National Environmental Research Institute
- The South Bank University, United Kingdom
- The Technical Research Centre of Finland
- The Department of Fire Safety Engineering, Lund University, Sweden
- The Swedish National Testing and Research Institute
- The Swedish Defence Research Establishment

The main objectives of the TOXFIRE project were to develop a basis for two guideline documents in relation to fires in chemical warehouses, namely: guidelines for fire safety engineers and guidelines for fire brigades. In parallel with these, a quick decision system to be used by the fire chief in the case of a chemical fire was developed. To achieve these objectives, the project was divided into a number of work packages. An overview of the project is presented in Figure 1.

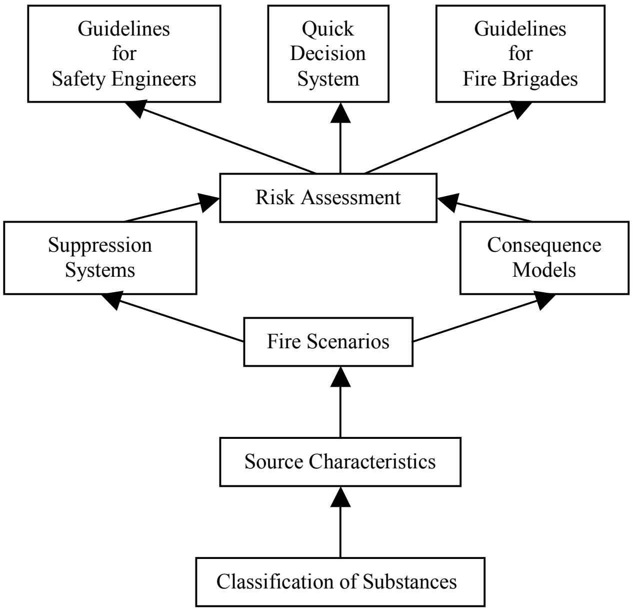

Figure 1. Overview of the structure of the TOXFIRE project.

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The project is summarised in the final report by Petersen and Markert [2], where a comprehensive list of publications emanating from the project is included.

Parallel to the projects mentioned above, a number of other projects were also initiated and financed by the CEC. Among these were:

- MISTRAL I and II: Modelling of Transport and Environmental Impact of Fires. Coordinated by J-C. Malet, IPSN Cadarache, France.
- Major Hazards Arising from Fires in Warehouses and Chemical Stores.
  Coordinated by S. Jagger, HSE, UK.
- Dispersion from Strongly Buoyant Sources.
  Coordinated by D. Webber, AEA Technology, UK.
- Mitigation of Hazardous Fire Radiation by a Water Spray Curtain.
  Coordinated by J. Liéto, ITC Lyon, France.

The work presented in this dissertation is restricted to the experimental part of the TOXFIRE project and referred to in Figure 1 as Source Characteristics.

The objective of this dissertation is to give a general introduction to the production of combustion gases during fire experiments with special emphasis on chemicals containing hetero-atoms such as chlorine, nitrogen and sulphur. The results from the TOXFIRE project serve as a reference for the theories presented here.

2 Fire scenarios

A chemical warehouse fire is likely to occur in a building considerably larger than an ordinary test room. Unfortunately, it is economically impossible to study a fire under controlled conditions on such a large scale. Therefore, it is necessary to employ scaling in order to obtain the relevant information. Thus, a methodology must be established for determining combustion properties based on small-scale tests, which can then be translated into real-life scales. In the experiments performed in the TOXFIRE project four different scales were employed: micro, small, medium and large scale [2].

Micro-scale experiments
The DIN 53436 furnace was used for the micro-scale combustion experiments. The DIN furnace set-up is presented in Figure 2a. The set-up consists of a quartz tube (length 1 m, diameter 4 cm) and a movable (0.01 m/60 s) annular electric oven enclosing a section of the tube. The sample, 1-3 g, was divided between 24 small vessels in a 0.4 m quartz boat. Air was flushed through the quartz tube during the experiment and transported the combustion products into a Fourier Transform Infra-Red (FTIR) spectrometer for analysis. Experiments were performed at 500°C and 900°C and under three different ventilation conditions, 100 l/h, 50 l/h and 50 l air/h mixed with 50 l nitrogen/h. The conditions were chosen to simulate non-flaming decomposition and fully developed fires at different degrees of ventilation. The micro-scale experiments were performed at Risø National Laboratory in Denmark, referred to as Risø below.

Small-scale cone calorimeter
Small-scale experiments were performed in a modified, ventilation-controlled cone calorimeter, see Figure 2b. These experiments were conducted at the Technical Research Centre of Finland (VTT). The sample and a load cell were placed in an enclosure in which the amount of oxygen available for combustion could be varied by adjusting the flow rates of the input gases and/or their oxygen concentration. The air and nitrogen flow rates could be adjusted between 0.5 and 4.0 l/s. The atmosphere in the cone calorimeter was 12.5, 15 or 21% O_2 in the TOXFIRE experiments and the amount of sample burned was 10-20 g.

Medium-scale experiments
The medium-scale combustion tests were performed in a stainless steel combustion chamber fitted inside a furnace. The internal dimensions of the chamber were 0.75 m (width), 1.1 m (depth) and 0.8 m (height), which is approximately 1/3 of the standard ISO room corner test. The amount of sample burned was 0.5-1 kg. The opening height of the chamber was adjustable in order to allow the ventilation conditions to be changed. It was also possible to heat the walls and the ceiling of the chamber so that external heat could be applied. The overall configuration of the equipment is shown in Figure 2c. The experiments were performed at the Department of Fire Safety Engineering, Lund University, Sweden (LTH).

Indoor large-scale fire tests
The large-scale experiments were performed inside a lightweight concrete room with dimensions in accordance with ISO 9705, see Figure 2d. The experiments were conducted at the Swedish National Testing and Research Institute (SP). The room had one opening: 0.8 m x 2 m. Changing the height of the opening altered the ventilation conditions. Heights of 0.9 m, 0.7 m, 0.6 m and 0.5 m were used during the experiments. The sample, 50 kg, was placed in

pans of different sizes (0.5 m^2-1.4 m^2), the aim of which was to obtain about the same total heat release rate, irrespective of the substance being combusted.

Expressed as the fuel ratios, the scaling factors in the TOXFIRE experiments were 1:10:500:50,000.

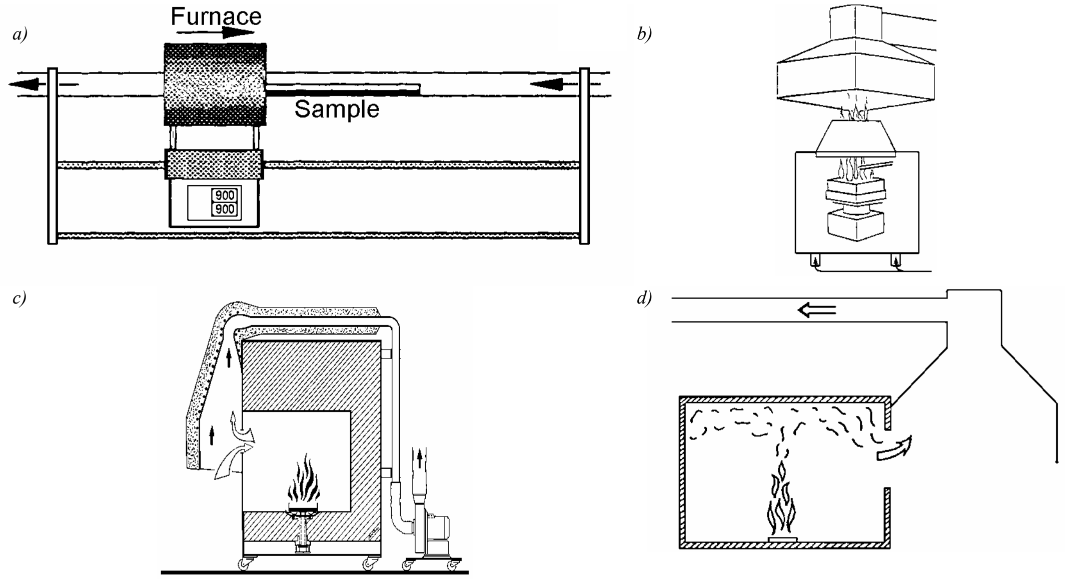


Figure 2. The experimental set-ups employed in the TOXFIRE project: a) micro-scale, a DIN furnace, b) small-scale, the cone calorimeter, c) medium- scale, the 1/3 ISO room and d) large-scale, the ISO room.

3 Experimental techniques

A fire source can be characterised by a large number of parameters, such as the evolution of combustion products, temperature, radiation, equivalence ratio, effective heat of combustion and the residence time for various components inside the combustion enclosure. The ability to measure these parameters in a representative way is fundamental in order to produce usable results from fire experiments. A résumé over available measuring techniques is given below.

3.1 Gas and particle concentrations

It is essential to determine concentrations of combustion products, the amount of the original substance that has survived the fire (survival fraction) and the amount of soot in the combustion gases leaving the fire when assessing the fire hazard of a substance or material. Gas concentrations can be measured on-line during an experiment or estimated from samples taken intermittently during certain periods of the experiment. Sometimes it is not feasible to perform these kinds of sampling, in which case grab samples can be taken and analysed qualitatively or quantitatively.

Table 1. Measurement techniques used for gas analysis in the TOXFIRE project.

Experimental set-up	**Measured species**	**Measurement principle**	**Sampling position**
Micro-scale DIN furnace	CO_2, CO, $COCl_2$, HCN, N_2O, NO, NO_2, SO_2, HCl	FTIR	On-line from the exhaust tube
	Organic combustion products	GC-MS (gas chromatography – mass spectrometry)	Grab samples from the exhaust tube
Small-scale Cone calorimeter	O_2, CO_2, CO, HCN, NO_x, SO_2, HCl	FTIR	On-line from the exhaust tube
	Organic combustion products	GC-MS	Grab samples from the exhaust tube
Medium-scale experiments	O_2	Paramagnetic	On-line in the exhaust duct
	CO_2/CO	IR absorption	
	NO_x	Chemiluminescence	
	Unburned hydrocarbons	Flame ionisation	
	Soot (absorbance)	Optical measurement	
	HCl, SO_2	Ion chromatography	Intermittent wet sampling from the exhaust duct
	Organic combustion products	GC-MS, flame ionisation	Grab sampling from the exhaust duct
	Soot (particles)	Collection of particles on filters	Intermittent sampling from the exhaust duct
Indoor large-scale fire tests	CO_2/CO	IR absorption	On-line in the exhaust duct
	NO_x	Chemiluminescence	
	Unburned hydrocarbons	Flame ionisation	
	O_2	Paramagnetic	On-line in the opening
	NO, NO_2, NO_x	Chemiluminescence	
	Unburned hydrocarbons	Flame ionisation	
	H_2O, CO_2, CO, HCl, SO_2, HCN, NH_3	FTIR	
	Organic combustion products	GC, LC (liquid chromatography)	Grab sampling in the opening
	Soot (particles)	Collection of particles on filters	Intermittent sampling from the opening

During the TOXFIRE experiments two different methods were used for on-line analysis. Either conventional on-line instruments were used to determine O_2, CO_2, CO, NO_x and the amount of unburned hydrocarbons, or all these gases (except O_2 and unburned hydrocarbons) were measured with the FTIR technique. For special compounds other techniques were also employed. A list of the measurement techniques used in the different set-ups is presented in Table 1.

Conventional dedicated instruments have been used for the on-line analysis of combustion products, but recently many researchers have adopted the FTIR technique. This technique has the advantage that many species can be analysed simultaneously, however, for some compounds the peaks in the spectrum overlap, which may reduce the accuracy of the measurements.

The accuracy of the conventional on-line instruments was of the order of ± 1% of full scale of the measuring range. The measuring accuracy is highly dependent on the quality of the calibration of the instruments and it is important that the measured concentrations are within the calibrated concentration range. The different types of instruments require various forms of preparation of the combustion gases prior to introduction into the instrument. Pre-treatment may involve drying the gases to avoid interference by water, different kinds of filtering techniques to free the gases from particles, or cooling of the gases to condense components with low boiling points.

The FTIR technique offers the possibility to determine the concentrations of a large number of toxic compounds in combustion gases using one instrument. The preparation of the gases before entering the FTIR instrument includes filtering to free them from particles. Heated filters and sampling lines are used to avoid the condensation of any component. FTIR analysis requires extensive calibration for the expected combustion components over a wide range of concentrations. Calibration is also necessary for compounds that may give spectral overlap. Water is such a compound, present in combustion gases. The results from the FTIR analysis are given as spectra, which have to be evaluated. There are different methods of doing this. Standardised procedures have been presented, such as NT FIRE 047 [3], which was used by VTT in small-scale tests in the TOXFIRE project. In accordance with the NT FIRE 047 standard, the sampling line and the IR absorption cell were heated to 130°C; nothing is stated in the standard about heating the filters. In the equipment used in the large-scale experiments the filter was heated to 180°C and the sampling line to 200°C. The IR absorption cell was maintained at a temperature of 150°C. A thorough evaluation of the use of the FTIR technique for combustion gas analysis was carried out within the SAFIR project. A summary of the findings is presented by Hakkarainen et al. [4].

Combustion products can be characterised and presented in a number of ways. The results presented here are given as yields, y_i. The yield of a specific component is defined as the ratio between the mass of the component produced, m_i, and the mass loss of the original substance, m_{fuel}.

$$y_i = \frac{m_i}{m_{fuel}} \qquad \text{[Eq. 1]}$$

For the calculation of yields, measurements of the mass loss from the burning substance are needed together with measurements of the mass flow in the duct or opening where the gas sample is taken. The latter is needed since the combustion products are measured as concentration, in a flow of gases and, therefore, the total flow of gases must be known in order to calculate the mass of the compound in question.

3.2 Temperature and rate of heat release

The temperature inside a fire compartment and in the combustion gases leaving a fire is an important parameter when assessing fire hazards. The temperature is usually measured with thermocouples of varying thickness and material. A thin thermocouple is less sensitive to radiation and should therefore give a better result but on the other hand, it is more susceptible to physical damage.

The heat released by a material, normalized to the fuel mass loss can be used in fire assessment models and in risk analysis to predict the contribution of a particular material or substance to the overall fire hazard. In order to ignite a material a minimum heat flux is needed. This minimum heat flux, together with the heat release rate from the material being studied can be measured in a number of different kinds of equipment. The Ohio State University (OSU) heat release rate apparatus, the Factory Mutual Research Centre (FMRC) flammability apparatus and the cone calorimeter are frequently used pieces of equipment. The main principle of these instruments is to expose a horizontal sample, in the OSU apparatus a vertical sample to various heat fluxes until the minimum heat flux is found at which the material is not ignited following exposure for a certain period (minutes). The heat release rate is determined by choosing a heat flux above the minimum heat flux for ignition and measuring the heat released by the material. The mass loss, or the total amount of vapour leaving the apparatus, is also measured and used to normalize the heat release rate since this quantity can be used for scaling purposes.

3.3 Equivalence ratio

There are many reasons why accidental fires can be a threat to life and to the environment. Fires in which the amount of oxygen available for combustion is low, thus leading to an under-ventilated or oxidizer-controlled fire, can be especially hazardous and life threatening. The production of CO is promoted by a low oxygen concentration, and as the human body preferentially takes up CO, which is toxic, the threat to life increases as the CO concentration increases. The production and composition of fire gases are also influenced by the amount of oxygen available; more pure pyrolysed products and less combustion products being formed in a low-oxygen atmosphere. For these reasons, it is vital to be able to measure or estimate the degree of ventilation during the course of a fire. The degree of ventilation can be defined as the actual fuel/oxygen ratio compared with the stoichiometric fuel/oxygen ratio, as in Eq. 2. When the overall combustion process is studied the ratio is usually called the Global Equivalence Ratio, GER.

$$\phi = \frac{\dot{m}_{fuel} / \dot{m}_{oxygen}}{\left(\dot{m}_{fuel} / \dot{m}_{oxygen}\right)_{stoich}} \qquad \text{[Eq. 2]}$$

A thorough presentation of the GER concept is given by Pitts [5]. The GER can be determined in well-controlled experiments where measurements of mass loss, as well as fuel and airflows, can be made. In many experimental situations this is not easily achievable and the need for other techniques is apparent. Optical techniques using laser-induced fluorescence (LIF) and Rayleigh scattering are suitable for measuring the equivalence ratio under certain conditions [6, 7]. However, LIF measurements include complex corrections for the sensitivity of the signal to collision partners and the use of Rayleigh scattering is limited to cases in which no macroscopic particles (soot) are present.

Babrauskas et al. presented an instrument suitable for measuring the equivalence ratio using a probe technique [8]. This apparatus has been developed further in order to make it more versatile and easier to use in non-laboratory environments. The apparatus is referred to as a phi-meter since the Greek letter phi, ϕ, is frequently used to denote the equivalence ratio. The design of the phi-meter and results comparing measurements with the phi-meter with calculated values are presented in Paper I. Measurements of the equivalence ratio with a mass spectrometer are also presented in Paper I.

In addition to measuring the GER the phi-meter can be used to determine the local equivalence of a specific location inside a room or in a flame. In order to investigate the versatility of the methods presented in Paper I, experiments were performed with a number of fuel mixtures of propane/air and propene/air. Combustion gases from a diffusion flame of propene were also analysed. Propene was chosen for the latter experiments because of its ability to produce large amounts of soot under low-ventilation conditions. An example of the results is given in Figure 3.

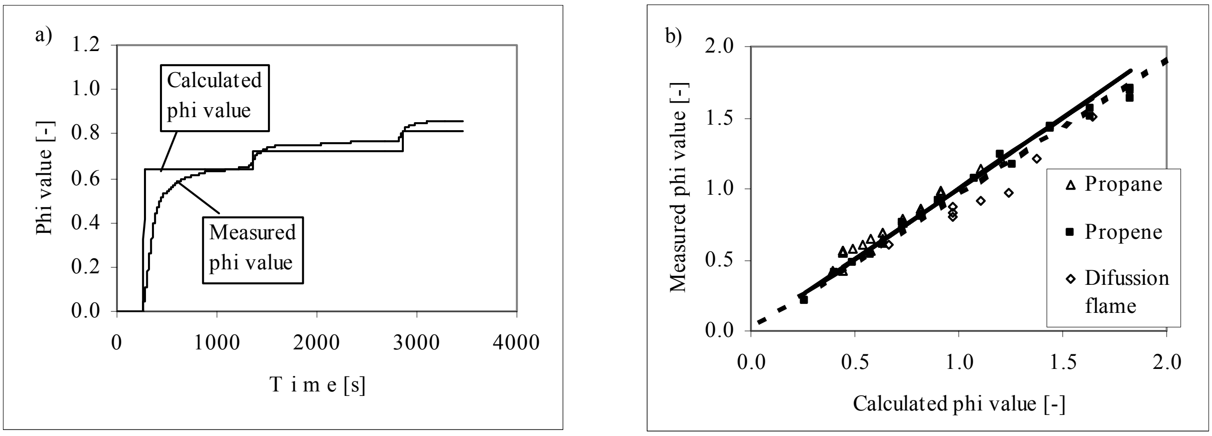


Figure 3. a) Measured and calculated phi values from an experiment on the combustion of propane, as a function of time. b) Experimental versus calculated phi values for measurements with the phi-meter. Results for propane, propene and a propene diffusion flame are shown in the diagram. The solid straight line represents the ideal results when measured and calculated values are equal and the dotted line represents the result of linear regression which gives a constant of determination $R^2=0.950$.

For the measurement of the GER in enclosure fires Gottuk [9] used another approach. A special enclosure was constructed so that air entered only through an inlet duct located beneath the floor of the enclosure. Narrow openings along the edge of the floor allowed air to be drawn into the enclosure. This made it possible to measure the airflow into the enclosure. The outflow of combustion gases was through a single window in one of the sides of the enclosure. It was ensured that no air was entrained through the window. The combustion gases were collected in a hood and drawn through an exhaust duct. The GER was determined by measuring the mass loss of the sample and the air mass inflow and dividing their ratio by the ratio for stoichiometric burning.

Beyler [10] introduced yet another method. The fuel was allowed to burn freely under a hood without any surrounding structures, and the combustion gases were trapped inside the hood. Eventually, the hood was filled with combustion gases and a hot upper layer was formed. The fire was allowed to burn long enough for steady-state behaviour to be attained in the upper layer. Concentration measurements of different combustion products were also made in the upper layer. The GER was then determined by measuring the mass of gas in the upper layer derived from the mass of fuel divided by the mass of gas introduced from the surrounding air and then normalized by the stoichiometric ratio.

For ventilation-controlled fires the fire conditions can be described by the local equivalence ratio:

$$\phi = \frac{S \cdot \dot{m}'' \cdot A}{\dot{m}_{air}} \qquad \text{[Eq. 3]}$$

where S is the stoichiometric ratio of the mass of air to fuel in kg/kg, $\dot{m}''$ is the mass loss rate in kg/m^2·s, A is the exposed area of the material in m^2 and $\dot{m}_{air}$ is the mass flow of air in kg/s. Generalised relationships between mass fractions of major combustion products such as O_2, CO_2 and CO as a function of the local equivalence ratios for laminar diffusion flames of hydrocarbons are presented in the literature, see e.g. Sivathanu & Faeth [11]. The relationships presented suggest that for fuel-lean conditions the concentrations of major combustion products are close to equilibrium concentrations for equivalence ratios up to 1. This concept was developed further by Tewarson [12] and applied to fires involving polymeric materials. The generation of combustion products was measured for various equivalence ratios in the FMRC flammability apparatus. The ratio between the yield per unit mass of the studied species under ventilation-controlled conditions and the yield under well-ventilated conditions is presented as a function of the equivalence ratio. For equivalence ratios below 1 the yield ratio is close to 1, but for larger values of the equivalence ratio the yield ratio increases for reduction products and decreases for oxidation products. The ratio for oxidation products seems to be independent of the composition of the material tested, whereas the ratio for reduction products tends to depend on the chemical composition of the material [12]. The correlations for CO_2, Eq. 4, and CO, Eq. 5, are presented below.

$$\frac{(y_{CO_2})_{vc}}{(y_{CO_2})_{wv}} = 1 - \frac{1.00}{\exp(\phi / 2.15)^{-1.2}} \qquad \text{[Eq. 4]}$$

$$\frac{(y_{CO})_{vc}}{(y_{CO})_{wv}} = 1 + \frac{\alpha}{\exp(2.5 \cdot \phi^{-\xi})} \qquad \text{[Eq. 5]}$$

The index *vc* denotes ventilation-controlled conditions and *wv* well-ventilated conditions. α and ξ are correlation coefficients that depend on the chemical structure of the material being tested. The “Tewarson” approach was applied to the chemicals studied in the TOXFIRE project and some results are presented in Section 4.2.

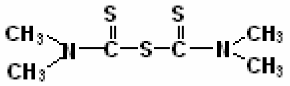
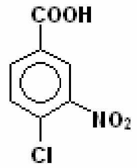
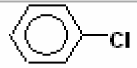
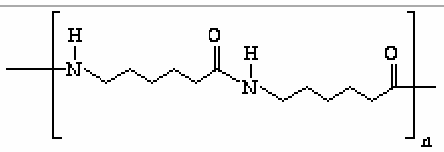
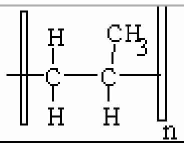
4. Experimental results

4.1 Gas and particle concentrations

Many attempts have been made to correlate measurements of combustion gas concentrations in the fire plume with those in the upper layer in an enclosure fire with GER [12, 13, 14]. Pitts [15], for instance, introduced an engineering approach for estimating carbon monoxide formation in enclosed fires. The major conclusions of earlier studies can be summarised as follows:

- Major flame species can be correlated in terms of GER.
- The generation of CO, soot and unburned hydrocarbons is considerably greater, and of CO_2 considerably lower, under fuel-rich conditions than under fuel-lean conditions.
- Different mechanisms can affect reaction rates. Quenching of a turbulent fire plume upon entering a fuel-rich upper layer, mixing of oxygen directly into a fuel-rich, high-temperature upper layer with subsequent reaction, pyrolysis in a high-temperature, oxygen-vitiated environment or approaching full equilibrium combustion product concentrations in a fuel-rich, high-temperature upper layer can considerably alter the composition of the combustion gases.

Table 2. Substances studied in the TOXFIRE project.

Chemical	**Formula**
Heptane Heptane C_7H_{16}	CH_3-CH_2- CH_2 -CH_2 -CH_2 -CH_2 –CH_3
Tetrametylthiuram monosulphide TMTM $C_6H_{12}N_2S_3$	
4-Chloro-3-nitro-benzoic acid CNBA $C_7H_4NO_4Cl$	
Chlorobenzene CB C_6H_5Cl	
Nylon 6,6 Nylon -$C_{12}H_{22}N_2O_2$-	
Polypropylene PP -C_3H_6-	

Tolocka et al. [16] have also shown experimentally that the yields of combustion gases are dependent on GER and temperature. They presented experimental results and the dependence of GER on combustion products confirming former results [13], i.e. that CO increases with GER, and CO_2 increases with GER up to GER=1 and then decreases. They also found a pronounced temperature dependence indicating that GER is not the only parameter that can be used as a scaling factor.

The correlations presented in the literature are normally between hydrocarbons and plastic materials. In some cases, polymers containing halogen atoms are included. The substances that were examined in the TOXFIRE project were of a more complex nature. See Tables 2 and 3 for a description of the materials and their characteristics.

Table 3. Characteristic variables for the substances studied in the TOXFIRE project.

Substance	**M_w [kg/kmole]**	**ΔH_c [kJ/kg]**	**r_i [kg_{air}/kg_{fuel}]**
Heptane	100.2	$44.6 \cdot 10^3$	15.11
TMTM	112.6	$25.7 \cdot 10^3$	7.91
CNBA	208.4	$13.7 \cdot 10^3$	3.92
CB	201.6	$26.2 \cdot 10^3$	8.54
Nylon	152.6	$28.9 \cdot 10^3$	10.02
PP	226.4	$43.3 \cdot 10^3$	14.7

4.2 Production of CO and CO_2

In the experiments involving organic fuels containing hetero-atoms observations regarding the dependence of the yields of CO_2 and CO on the GER were similar to those reported by other researchers. This is illustrated by the results presented in Figure 4a where the ratio between the CO_2 yields and the maximum CO_2 yield, 2.06 kg/kg, for experiments with nylon, from three different experimental series are shown as a function of the GER. The correlation according to Tewarson [12] is also shown. In experiments with chlorine-containing substances this relation was much weaker, as can be seen for CNBA in Figure 4b. For CNBA the maximum yield of CO_2 was set to 1.53 kg/kg. As illustrated in Figure 4b the Tewarson correlation does not fit the data for this chlorine-containing substance. This is discussed in Chapter 5. The yield of CO for PP is presented as the ratio of measured CO yield to the CO yield under well-ventilated conditions as a function of the GER in Figure 5a. The maximum yield of CO for well-ventilated conditions was assigned a value of 0.03 kg/kg. In Figure 5b the CO yield versus GER is presented for CB with a yield of CO for well-ventilated conditions of 0.022 kg/kg. For PP there is a strong dependence between the GER and the yield of CO, but this is not as evident for CB, especially regarding the results from the experiments in the cone calorimeter (VTT).

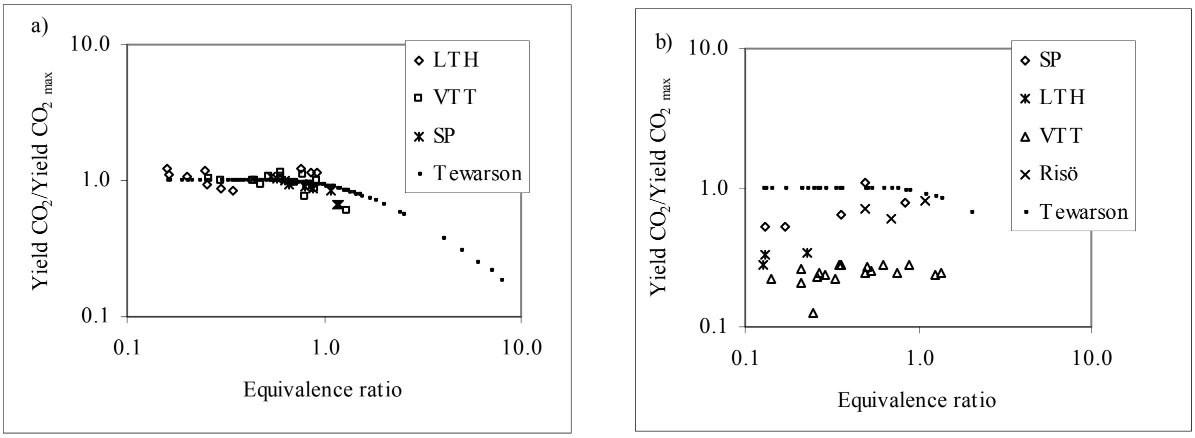


Figure 4. a) Ratio of the yield of CO_2 to the maximum yield of CO_2 for well-ventilated conditions in experiments with nylon. The dotted line shows the Tewarson correlation. b) Ratio of the yield of CO_2 to the maximum yield of CO_2 for well-ventilated conditions in experiments with CNBA. The dotted line shows the Tewarson correlation.

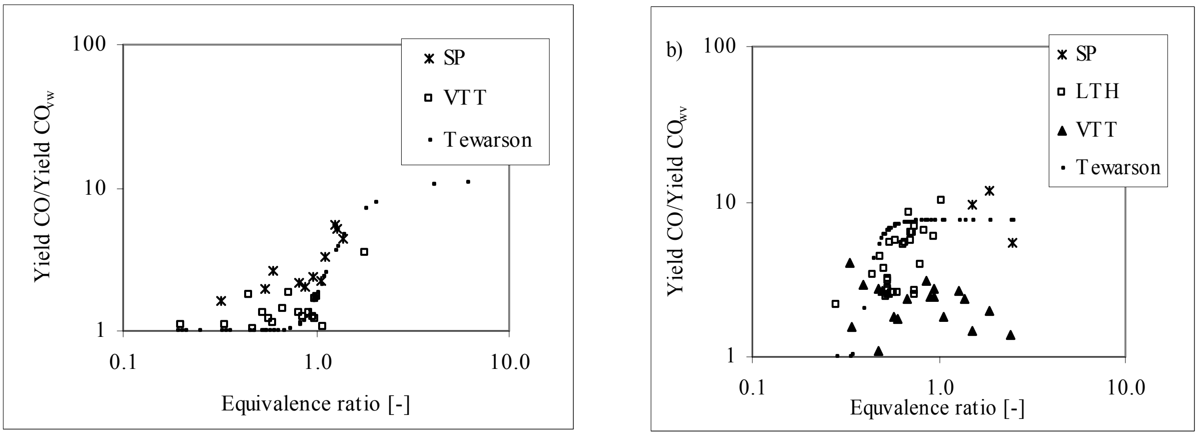


Figure 5. a) Ratio of the yield of CO to the CO yield for well-ventilated conditions during experiments with PP. The dotted line shows the Tewarson correlation. b) Ratio of the yield of CO to the CO yield for well-ventilated conditions during experiments with CB. The dotted line shows the Tewarson correlation.

4.3 Production of soot and hydrocarbons

In fires involving organic substances such as those studied in the TOXFIRE project, varying amounts of unburned hydrocarbons and soot are released with the fire gases. Low-molecular-weight hydrocarbons can be measured on-line with conventional methods, higher-molecular-weight hydrocarbons have to be analysed with more sophisticated methods such as GC-MS. It is generally expected that a decrease in the ventilation will lead to an increase in the production of smoke and unburned hydrocarbons. For the substances PP and nylon the production of low-molecular-weight unburned hydrocarbons follows the expected pattern. As can be seen in Figure 6a the yields of unburned hydrocarbons increase as the degree of ventilation decreases. For CB, which contains chlorine, the results are different, Figure 6b, the trend is quite the opposite. Possible explanations for this converse behaviour are presented in Chapter 5.

The combustion of organic compounds can give rise to substantial amounts of smoke and unburned hydrocarbons. As mentioned above, the low-molecular-weight hydrocarbons can be measured on-line with a flame ionisation detector. Polymers behave somewhat differently upon heating from many other organic substances. Since they are made up of long chains of monomers they tend to break into rather large fragments consisting of a number of monomer molecules and combinations of monomer remnants before they are completely oxidized. These large molecules can be analysed either directly in gas samples taken from the combustion gases or on soot samples, which must be extracted into solution and then analysed. Such analysis can be performed using on a GC-MS spectroscopy. This type of analysis may be qualitative or quantitative. Results from such analysis within the TOXFIRE project are presented in Paper II. It was found that for some substances part of the parent substance was not affected at all by combustion, and it remained completely unchanged throughout the combustion process. This part was called the survival fraction. For CB survival fractions as high as 2-8% were detected in the cone calorimeter and in the medium-scale room experiments.

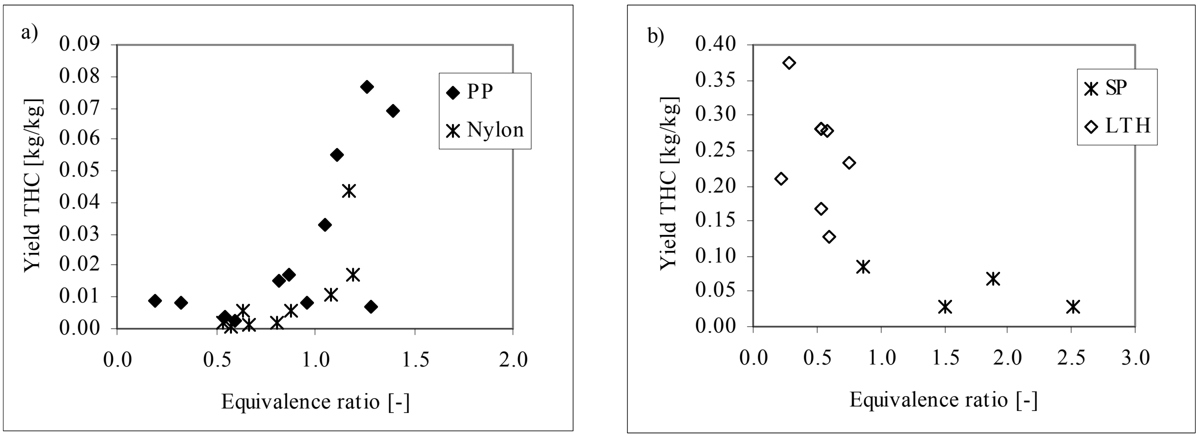


Figure 6. a) The yield of unburned low-molecular-weight hydrocarbons is presented as a function of GER for experiments with PP and nylon. The PP experiments were performed in the large-scale ISO room and the nylon experiments in the large-scale ISO room and in the medium-scale combustion chamber. b) The yield of unburned low-molecular-weight hydrocarbons is presented as a function of GER for experiments with CB.

Smoke is produced in almost all fires and can cause considerable damage to property and the environment, as well as injury to people. It is a danger to people because of its light-obscuring properties and its toxic properties. The soot itself is not the biggest problem but toxic substances are often adsorbed on to the soot particles and are consequently inhaled together with the soot. Smoke production can be measured and presented in a number of ways. It is common practice in fire experiments to measure the light-obscuring capacity of the combustion gases either with a lamp and a photocell or with laser techniques. The results can be expressed as optical density or as an extinction coefficient. The extinction coefficient, *k*, expressed in m^{-1}, can be defined as in Eq. 6.

$$k = \left(\frac{1}{L}\right) \cdot ln\left(\frac{I_0}{I}\right) \qquad \text{[Eq. 6]}$$

where L [m] is the beam length through the smoke, I_0 [-] is the light intensity without smoke and I [-] is the light intensity during the fire experiment.

The extinction coefficient can also be defined as in Eq. 7 from reference [17]:

$$k = \sigma_s \cdot C \qquad \text{[Eq. 7]}$$

where σ_s is the extinction area per unit mass of soot produced [m^2/kg] and C is the mass concentration of the smoke particles [kg/m^3]. The smoke extinction area can also be expressed per unit mass of pyrolysed fuel, σ_f, giving the specific extinction area, computed on a fuel-mass-loss basis [m^2/kg]. The two extinction areas σ_s and σ_f are related via ε, the fraction of fuel mass loss converted to soot or, as it is often called, the soot yield.

$$\sigma_f = \varepsilon \cdot \sigma_s \qquad \text{[Eq. 8]}$$

σ_f is used to characterise the smokiness of a substance. A high value of σ_f implies that a high amount of smoke is emitted per kg of substance burned. σ_s, on the other hand, gives the light attenuation per kg soot particles produced. The value of σ_s is rather constant, about 10, 000 m^2/kg, for flaming combustion of organic fuels [18].

σ_s can also be determined according to Eq. 9 from measurements in a duct and from samples of soot collected on filters during experiments.

$$\sigma_s = k \cdot (V \cdot (273 + T_{duct}) / 273) / m_{soot} \qquad \text{[Eq. 9]}$$

V is the volume of gas [m^3] that has passed through the filter, T_{duct} [°C] is the temperature in the duct and m_{soot} is the amount of soot [kg] that has been collected on the filter during the measuring period. The soot production can also be given as a yield in [kg/kg] i.e., kg soot produced per kg substance burned. The smoke production, S_{pr}, expressed as mass per unit time, can be calculated as in Eq. 10.

$$S_{pr} = k \cdot \dot{V} \cdot ((T_{duct} + 273) / 273) \cdot (1 / \sigma_s) \qquad \text{[Eq. 10]}$$

The soot yield can then be calculated as the ratio between S_{pr} and σ_s. The values of σ_s and σ_f for some of the substances studied in the TOXFIRE project are presented in Table 4. These values are in good agreement with values of smoke extinction areas, σ_s, presented by Babrauskas and Mulholland [18].

Table 4. Typical smoke data from experiments in the medium-scale combustion chamber (LTH)

Substance	σ_s **[m^2/kg]**	σ_f **[m^2/kg]**	ε **[kg/kg]**	ϕ **[-]**
TMTM	670	13	0.02	0.7
CNBA	8300	1250	0.15	0.2
CB	9500	1800	0.19	0.8
Nylon	9500	1330	0.14	0.2

4.4 Production of other combustion gases

Nitrogen-containing substances can form HCN, N_2 and nitrogen oxides (NO_x) during combustion. HCN and NO_x are potentially toxic and therefore it is of interest to investigate which conditions promote the production of the different gases. NO_x can be formed through a number of reactions. The reaction can be with the nitrogen in the air by two main pathways giving “thermal or Zeldovich NO” and “prompt or Fenimore NO”. The former is favoured at very high flame temperatures, which are less likely during uncontrolled combustion, especially for CNBA, which burns rather poorly. Prompt NO formation is due to the reaction of free CH radicals with N_2 at the flame front. This probably made a minor contribution to the overall NO_x yields found in these experiments and the major part of the NO_x emissions will be due to the nitrogen in the fuel.

It is known that HCN formed during combustion can be consumed if there is sufficient oxygen and if the temperature is sufficiently high. This may results in different nitrogen oxides, N_2 and CO or CO_2. In experiments with nylon and TMTM an increase in the HCN yield with increasing GER was found, but for the chlorine containing CNBA the behaviour was the opposite. The production of nitrogen oxides follows the same pattern for all substances investigated. A decrease in NO_x with increasing GER was found for both the chlorine-containing substances as well as for those without chlorine. Only the sum of nitrogen oxides was measured so no conclusions can be drawn as to the formation of the different types of nitrogen oxides.

Chlorine-containing substances are potential sources of HCl in a fire. PVC is a polymer that is often present in modern buildings since it is used in many electric appliances such as cables. When PVC is heated it gives off considerable amounts of HCl, which is a corrosive gas, and can cause damage to property even when it is present in small amounts. It is also highly irritating and toxic to humans. HCl is produced from PVC even at low temperatures, (200°C), and increasing temperature does not seem to increase the production of HCl [19]. Other chlorine-containing substances can be expected to release HCl, but the temperature at which HCl is released and the extent to which chlorine is given off as HCl vary depending on their chemical structure. Two chlorine-containing substances, CB and CNBA, were included in the TOXFIRE project and they behaved differently from PVC. For CB a high temperature, greater than 900°C, is needed to cause a high degree of HCl release. This high temperature is reasonable, as the dissociation energy for the carbon—chlorine bond in CB is very high. The C—Cl bond dissociation energy in PVC, for example, is much lower. For both CNBA and CB the production of HCl seems to be, in principle, independent of the equivalence ratio.

For substances containing sulphur, SO_2 can be expected to be the primary sulphur compound formed during combustion. This assumption was confirmed by the experiments on TMTM in the TOXFIRE experiments. It was found that the sulphur dioxide yield was about 100% at equivalence ratios less than 1, and decreased for ϕ values greater than 1. Other sulphur compounds than SO_2 can be formed and this was also confirmed by GC-MS analyses of gas samples from experiments on TMTM in the medium-scale experiments. The substances detected were mainly dissociation products of the original substance. A comprehensive list of substances detected is presented in Paper II.

5 Discussion and further work

In the TOXFIRE project four different scales were employed for fire tests. They represent not only different sizes of testing set-ups but also different fire scenarios.

The large-scale and the medium-scale experiments represent well-defined enclosure fires, where the ventilation conditions could be changed by changing the size of the opening and the amount of fuel introduced into the enclosure. Temperatures and combustion products could be measured both inside the compartment and in the gases leaving the enclosure. The intention of the TOXFIRE experiments was to perform experiments over a range of ventilation conditions. However, it proved difficult to achieve stable conditions under low ventilation conditions for the substances that required high temperatures or large heat fluxes for ignition. When these substances were eventually ignited the fires tended to be unstable and pulsating under conditions of low ventilation. Regarding gas sampling in the duct, it was essential that samples were taken during periods when no burning was taking place outside the enclosure.

The micro-scale experiments were performed in surroundings where the initial temperature and the combustion atmosphere were well defined. These parameters were changed during the course of the tests. The influence of the substance being studied on the temperature is not known during the test since the DIN furnace was kept at a constant temperature, but the sample was at ambient temperature when introduced into the furnace, which must influence the overall temperature. The combustion of the substance also contributes to the temperature change during the course of the test but the temperature inside the furnace was not monitored during the experiments. It is thus impossible to derive any correlations involving temperature from the micro-scale experiments.

The cone calorimeter is a well-established method for testing the combustion behaviour of materials and/or substances, as is the DIN furnace. The cone calorimeter used in the TOXFIRE project was a modified, ventilation-controlled version of the standard cone calorimeter. Thus, the composition of the atmosphere in the cone could be regulated so that either air or different mixtures of nitrogen/oxygen were fed into the cone enclosure, which gives a known composition of the gases entering the cone. The temperature in the gases surrounding the fire plume is, however, not known so no correlations involving temperature can be derived from the results from the cone calorimeter. Under low-ventilation conditions unreacted combustion gases were burned above the test chamber. In these experiments the amount of oxygen available for combustion exceeds the amount introduced into the enclosure and this affects the results of measurements of gas composition made in the duct above the enclosure.

During fire or combustion, materials and chemical substances cause the release of hazardous and toxic compounds. Naturally, the composition of the substance involved in the fire will influence the combustion products that are produced. In order to produce sulphur-containing smoke gases, the original compound must contain sulphur; the same applies for other hetero-atoms such as chlorine. The production of CO and CO_2 is mainly controlled by the amount of oxygen available, but the influence of temperature is also evident as in the production of nitrogen oxides. There are, however, substances for which this general assumption does not apply. In the TOXFIRE project this was found to be the case for chlorine-containing substances. They behave contrary to what is expected. As can be seen in Figures 4, 5 and 6 the production of CO, CO_2 and THC for the chlorine-containing substances CB and CNBA differs considerably from that of the non-chlorine substances. An explanation of this may be that chlorine-containing substances produce less heat during combustion, i.e. they have a low combustion efficiency. Because of this, chlorine has been widely used for fire retardant purposes. Theoretical explanations of why compounds containing chlorine or other halogens behave differently from other substances during fires have been proposed in literature [20,21].

In order to achieve ignition and sustained combustion of a solid or liquid fuel, a certain amount of heat must be available. This can be expressed in the form of a critical adiabatic flame temperature, typically 1700 K for common fuels, or as a minimum radiative heat flux necessary for sustained burning. An energy balance for the conditions at extinction of a flame can be written as in Eq. 11:

$$(f \cdot \Delta H_c - L_v) \cdot \dot{m}''_{cr} + \dot{Q}''_E - \dot{Q}''_L = 0 \qquad \text{[Eq. 11]}$$

where f is the fraction of heat produced that is transferred back to the fuel surface, ΔH_c is the heat of combustion for the fuel volatiles, L_v is the heat of gasification of the substance, $\dot{m}''_{cr}$ is the critical mass flux needed for sustained burning (or for extinction), $\dot{Q}''_E$ is the externally applied heat flux and $\dot{Q}''_L$ denotes the sum of all heat losses. All the factors in Eq. 11 are dependent on the composition of the burning substance. The factor f is normally between 0.1 and 0.4 for combustion in ambient air. Upon introducing halogens, f will decrease and the adiabatic flame temperature at the lower flammability limit will increase. The ability of halogens to lower the value of f and to increase the adiabatic flame temperature makes these elements useful as active ingredients in flame-retardants and in fire-suppressing agents. This may also provide an explanation as to why the chlorine-containing substances gave results differing from the rest of the substances tested.

The amounts of unburned hydrocarbons are very low for the chlorine-containing substances at high GER. There could be a number of explanations of this. Of course, it is possible that the amount of low-weight hydrocarbons decreases as the GER increases. It is also possible that heavier components are produced and that these cannot be detected with the method of analysis employed. This suggestion is supported by the amounts of original compound found after combustion. It is also possible that low-molecular-weight compounds containing, for example, chlorine, are being formed and that the flame ionisation detector is unsuitable for measuring such compounds.

The TOXFIRE project has provided a wealth of information about burning chemicals in different fire scenarios as regards combustion products, including soot formation. There is, however, still a need for more information on burning chemicals in order to be able to perform good hazard and risk assessments concerning, for instance, the storage of chemicals in warehouses and in connection with retail stores. What is lacking is the link between measured variables and the application in hazard and risk assessment. Some conclusions can, however, be drawn. The sulphur in substances containing sulphur will react completely to form SO_2 as long as there is oxygen available, and for chlorine-containing substances 50-

100% of the chlorine content will be found as HCl in the combustion gases. Predicting the formation of HCN from complex substances is much more uncertain. There is a considerable lack of knowledge about the reaction kinetics for complicated substances, and what happens in different fire scenarios where variables such as ventilation, temperature and residence time vary over time. Chemical reaction schemes are known for simple fuels, but for complex chemicals much information is still required. In addition, when a risk or hazard assessment is to be performed a number of substances, giving different combustion products, must be taken into consideration at the same time. Together with this, synergistic effects may also have to be considered.

Combustion products are predominantly analysed with conventional on-line instruments or with FTIR techniques. Intermittent sampling followed by analysis with GC-MS or other techniques is also commonly used. All these techniques are intrusive, which mean that samples have to be taken from a flow of combustion gases and then analysed. There are many problems involved with the handling of these gas samples. For example, they need to be filtered, heated, freed from certain components to avoid overlapping signals, and it can also be difficult to take a representative sample. If non-intrusive methods could be applied several of these problems could be avoided. Such methods exist, mainly optical techniques using, for instance, laser-induced fluorescence (LIF) or Rayleigh scattering [6, 7]. However, these techniques are not without problems and their application to fire situations needs to be developed. The introduction of non-intrusive techniques into the area of measuring combustion products from fires could be one way of increasing the possibility of measuring combustion products from fire experiments continuously and thus extending our knowledge on the production and spread of toxic compounds from fires.

References

1. Smith-Hansen, L., STEP – Combustion of Chemical Substances and the Impact on the Environment of the Fire Products, Final Report, Risö-R-765, 1994.

2. Petersen, K. E. and Markert, F., Assessment of Fires in Chemical Warehouses – An overview of the TOXFIRE project, Risø-R-932, 1999.

3. NT FIRE 047, "Combustible Products: Smoke Gas Concentrations, Continuous FTIR Analysis", Nordtest, 1993-05.

4. Hakkarainen, T., Mikkola, E., Laperre, J., Gensous, F., Fardell, P., Le Tallec, Y., Baiocchi, C., Paul, K., Simonson, M., Deleu, C., and Metcalf, E., "Smoke Gas Analysis by Fourier Transform Infrared Spectroscopy – Summary of the SAFIR Project Results", Fire. Mater. 24 (2000), 101-112.

5. Pitts, W. P., "The Global Equivalence Ratio Concept and the Prediction of Carbon Monoxide Formation in Enclosure Fires", National Institute of Standards and Technology Monograph 179, Gaithersburg, MD, 1994, 171 p.

6. Neij, H., Thesis "Fluorescence for Precombustion Diagnostics in Spark-Ignition Engines", ISRN LUTFD"/TFCP-41-SE, 1998.

7. Andersson, Ö., Thesis "Development and Application of Laser Techniques for Studying Fuel Dynamics and NO Formation in Engines", ISRN LUTFD"/TFCP-61-SE, 2000.

8. Babrauskas, V., Parker, W. J,. Mullholland, G. and Twilley, W. H., "The Phi Meter: A Simple, Fuel-independent Instrument for Monitoring Combustion Equivalence Ratio", *Rev. Sci. Instrum.* Vol 65, No. 7: 2367-2375 (1994).

9. Gottuk, D. T., "Generation of Carbon Monoxide in Compartment Fires", National Institute of Standards and Technology NIST-GCR-92-619, December 1992, 265 p.

10. Beyler, C. L., "Major Species Production by Diffusion Flames in a Two-layer Compartment Fire Environment", *Fire Safety Journal* Vol. 10, No. 1, 47-56 (1986).

11. Sivathanu, Y. R. and Faeth, G. M., "Generalized State Relationships for Scalar Properties in Nonpremixed Hydrocarbon/Air Flames", Combustion and Flame, Vol 82: 211-230 (1990).

12. Tewarson, A. "Generation of Heat and Chemical Compounds in Fires", SFPE Handbook 2nd ed. 1995, 3-53-124.

13. Pitts, W. M., "The Global Equivalence Ratio Concept and the Formation Mechanisms of Carbon Monoxide in Enclosure Fires", Prog. Energy Combustion. Sci. (1995), 197-237.

14. Pitts, W. M., " Application of Thermodynamic and Detailed Chemical Kinetic Modeling to Understanding Combustion Product Generation in Enclosure Fires", Fire Safety Journal 23 (1994), 271-303.

15. Pitts, W. M., "An Algorithm for Estimating Carbon Monoxide Formation in Enclosure Fires", Proceedings of the 5th International Symposium of The IAFSS, Melbourne Australia, 3-7 March 1997, 535-546.

16. Tolocka, M. P., Richardson, P. B. and Houston Miller, J., "The Effect of Global Equivalence Ratio and Postflame Temperature on the Composition of Emissions from Laminar Ethylene/Air Diffusion Flames", Combustion and Flame, (1999), 118:5221-536.

17. Östman, B. "Smoke and Soot" in Babrauskas, V. and Grayson, S. J., (ed.) "Heat Release in Fires", Elsevier Applied Science, England, 1992, 233-250.

18. Babrauskas, V. and Mulholland, G, "Smoke and Soot Data Determinations in the Cone Calorimeter", Proceedings of a Symposium on Mathematical Modeling of Fires and Related Fire Test Methods, New Orleans, LA, December 13, 1986, 83-104.

19. Smith-Hansen, L. and Haahr Jørgensen, K., ”Combustion of Chemical Substances and the Impact on the Environment of the Fire Products, Micro Scale Experiments”, Risø-R-651, 1992.

20. Rasbash, D. J., “Theory in the Evaluation of Fire Properties of Combustible Materials”, Proceedings of the Fifth International Fire Protection Seminar, Karlsruhe, Germany, 1976, 113-130.

21. Beyler, C., ”A Unified Model of Fire Suppression”, J. of Fire Prot. Engr., Vol 4, No 1, 1992, 5-16.

Determination of the equivalence ratio during fire, comparison of techniques

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ABSTRACT: Equivalence ratios have been determined with two different techniques. The first, called the phi-meter, is a modification of the phi-meter earlier presented by Babrauskas et al. [1], while the other utilises a mass spectrometer as the analysing instrument. Results are presented from experiments with both techniques and a discussion concerning the deviations from theoretically calculated results is presented. The two methods presented are possible candidates in situations where global and/or local equivalence ratios need to be measured. In its present conformation, the phi-meter gives more consistent results than the mass spectrometer approach but the latter can be considerably improved by using a mass spectrometer with better resolution.

KEYWORDS: Equivalence ratio, phi value, global equivalence ratio, phi-meter, mass spectrometer.

INTRODUCTION

There are many reasons why unwanted fires can be a threat to life and to the environment. Especially fires where the amount of oxygen available for combustion is low, thus leading to an under-ventilated or oxidizer-controlled fire, can be life threatening. The production of CO is promoted by a low oxygen concentration, and as CO is preferentially taken up by the human body the threat to life increases as the CO concentration increases. The production and composition of fire gases is also influenced by the amount of oxygen available; more pure pyrolysed products and less combustion products being formed in a low-oxygen atmosphere. For these reasons, it is vital to be able to measure or estimate the degree of ventilation during the course of a fire. The degree of ventilation can be defined as the actual fuel/oxygen ratio compared with the stoichiometric fuel/oxygen ratio, as in Eq. 1. When the overall combustion process is studied the ratio is usually called the Global Equivalence Ratio, GER. A thorough presentation of the GER concept is given by Pitts [2]. The GER can be determined in well-controlled experiments where measurements of mass loss, as well as fuel and airflows, can be made. In many experimental situations this is not readily achievable and the need for other techniques is apparent. Optical techniques using laser-induced fluorescence (LIF) and Rayleigh scattering are suitable for measuring the equivalence ratio under certain conditions [3, 4]. However, LIF measurements include complex corrections for the sensitivity of the signal to collision partners and the use of Rayleigh scattering is limited to cases in which no macroscopic particles (soot) are present.

Babrauskas et al. presented an apparatus suitable for measuring the equivalence ratio using a probe technique [1]. This apparatus has been developed further in order to make it more versatile and easier to use in non-laboratory environments. The apparatus is referred to as a phi-meter since the Greek letter phi, ϕ, is frequently used to denote the equivalence ratio. Depending on how the sample to be analysed is collected the measured value can be a local phi value or a global phi value. The results from measurements with the phi-meter are in this work compared with results from measurements with a mass spectrometer. In order to investigate the versatility of the methods, experiments were performed with a number of mixtures of propane/air and propene/air. Combustion gases from a diffusion flame of propene were also analysed. Propene was chosen for the latter experiments because of its ability to produce large amounts of soot under low-ventilation conditions.

$$\phi = \frac{\dot{m}_{fuel} / \dot{m}_{oxygen}}{\left(\dot{m}_{fuel} / \dot{m}_{oxygen}\right)_{stoich}} \qquad \text{[Eq. 1]}$$

For measurement of the GER in enclosure fires Gottuk [5] used another approach.. A special enclosure was constructed so that air entered only through an inlet duct located beneath the floor of the enclosure. Narrow openings along the edge of the floor allowed the air into the enclosure. This made it possible to measure the airflow into the enclosure. The outflow of combustion gases was through a single window in one of the sides of the enclosure. It was ensured that no air was entrained through the window. The combustion gases were collected in a hood and drawn through an exhaust duct. The GER was determined by measuring the fuel mass loss and the air mass inflow and dividing their ratio with the ratio for stoichiometric burning.

Beyler [6] introduced yet another. The fuel was allowed to burn freely under a hood without any surrounding structures. The combustion gases were trapped inside the hood. Eventually the hood was filled with combustion gases and a hot upper layer was formed in the hood. The fires were allowed to burn long enough for steady-state behaviour to be attained in the upper layer. Concentration measurements of different combustion products were made in the upper layer. The GER could be determined by measuring the mass of gas in the upper layer derived from the fuel divided by the mass of gas introduced from air and then normalised by the stoichiometric ratio.

EXPERIMENTAL

Different approaches have been used in order to measure the local equivalence ratio. In the first one here referred to as the phi-meter the local equivalence ratio is calculated from the measured O_2 - N_2 ratio. In the second one here referred to as the mass spectrometer method the local equivalence ratio is calculated from the measured N_2 - CO_2 ratio. In order to measure the GER in a room fire a phi-meter with a sampling probe mounted diagonally across the upper part of the enclosure opening was tested and compared with GER calculated from measurements of fuel mass loss rate and air inflow.

The general technique employed with the phi-meter and the mass spectrometer technique is to lead a flow of combustion gases through a heated catalytic bed, where remaining uncombusted fuel is burnt.

Choice of catalyst

In order two achieve complete combustion in the reactor, a sufficient supply of oxygen is necessary as well as the presence of an effective catalyst. A small investigation was undertaken two find a suitable catalyst and its optimal working temperature. Two different catalysts were tested in these experiments, as mentioned above; a platinum catalyst and another made of metal oxides of Al, Cu and Mn. Tests were carried out with methane, propane and propene. Methane was included since it is known that methane requires a higher temperature for combustion than the gases used in the other experiments reported here.

A sample of a mixture of fuel gas and air was drawn through the heated reactor in the same way as in the experiments for phi value determination. The gases leaving the reactor were analysed in a flame ionisation detector (Siemens Fidamat K, M52044) in order to detect any uncombusted hydrocarbons. The temperature of the reactor was varied from 50°C up to 800°C in steps of 50°.

Tests were run for all combinations of catalyst and gas. The results of these tests are presented in Fig. 1.

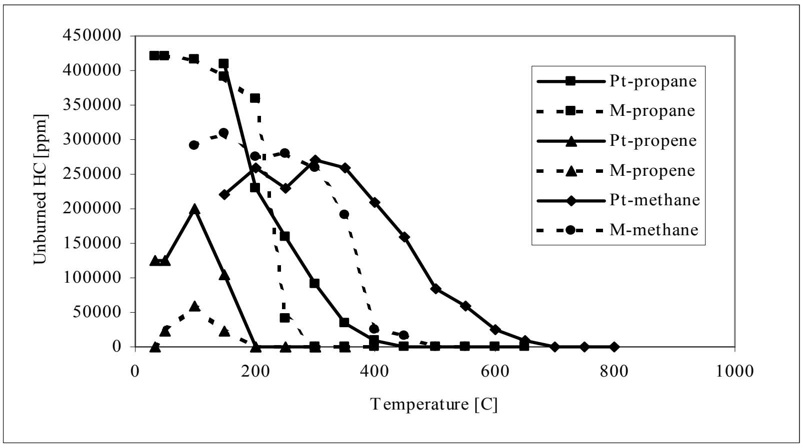

Figure 1. The catalytic efficiency dependency on the temperature for platinum (Pt) and metallic oxide (M) catalysts is presented for the combustion of methane, propane and propene.

As can be seen in the figure considerably lower temperatures were needed for the metal oxide catalyst than for the platinum catalyst for complete combustion of propane and methane. The results for propene are more difficult to interpret. Since no large difference can be seen in the optimal temperature for propene both catalysts should be acceptable for this fuel. The decision was taken to use the metal oxide catalyst at 350°C in most of the experiments with propane and propene. Some preliminary tests with propane were, however, carried out with the Pt catalyst at 350°C and 400°C. No significant differences could be seen between these experiments and similar experiments with metal oxide catalyst. The experiments with a propene diffusion flame gave the same results with both the Pt catalyst and the metal oxide catalyst. Experiments were conducted at 450°C, 550°C and 600°C. Increasing the temperature did not seem to have any influence on the combustion in the reactor since the ratio between the measured phi value and the calculated phi value remained the same.

Description of the phi-meter, using the nitrogen and oxygen balance

The phi-meter utilises the oxygen consumption technique, which is widely used to determine the heat release rate during combustion [7, 8, 9]. After the catalyst the gases are cooled and freed from CO_2 and H_2O. Thereafter, the oxygen content is measured with a paramagnetic oxygen analyser. An overview of the apparatus is given in Fig. 2. The original phi-meter was presented by Babrauskas et al. in 1994 [1].

The combustion gases are drawn through the phi-meter by a 12 V DC pump. In order to ensure that all the uncombusted gases are fully reacted, a known quantity of oxygen, measured with a mass flow controller (Aalborg Instruments, Denmark) is added just before the inlet to the reactor. The reactor with the catalytic bed is mounted in an electrically heated furnace that can be heated up to 1100°C. Temperatures in the range between 350 and 600°C were used in this series of experiments. Two different catalysts were tested, one made of silica beads covered with platinum, and the other of metal oxides of Al, Cu and Mn. The catalyst consisting of metal oxides was homogeneous with cylindrically shaped particles with a length of ~7 mm and a diameter of 3 mm. The platinum catalyst consisted of platinum-coated silica beads with a diameter of 4 mm.

After passage through the reactor, the gases ideally consist of CO_2, H_2O, N_2 and O_2. Should the fuel contain heteroatoms these will also be present in the gases leaving the reactor. The hot gases are cooled in an ice-water trap and then led through a series of absorbers consisting of silica gel to remove water, NaOH (s) and Ascarite to absorb CO_2, and finally through silica gel again to absorb any remaining water. The mass flow controller was used to ensure a constant flow of gases. Finally, the oxygen content was determined with a paramagnetic oxygen analyser; model PMA 10 (M&C Instruments, The Netherlands). Details of the equipment are presented in Table 1.

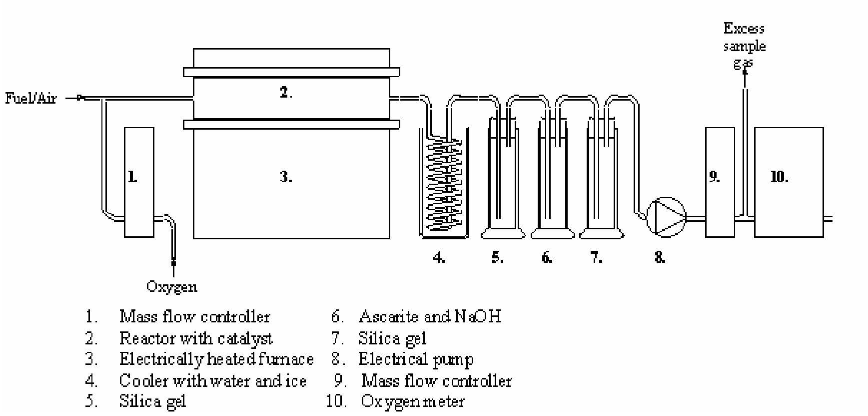

Figure 2. The overall layout of the experimental set-up, including the phi-meter.

Table 1 Details of the equipment in the phi-meter.

Reactor	**Mass flow controller**	**Catalyst**	**O_2 analyser**
Length: 300 mm Diameter$_{inner}$: 30 mm Material: steel	Aalborg Instruments Max pressure: 3400 kPa Gas: air Flow range: 0-1000 cm^3 Gas: O_2 Flow range: 0-500 cm^3 Accuracy: $\pm$1% of full scale	a) Pt beads Diameter: 4 mm b) Cylinders of Al, Cu and Mn oxides Diameter: 3.1 mm Length: 6.8 mm	M&C Instruments, PMA 10 0-100 vol% Accuracy: $\pm$0.1 vol%

One way to determine the equivalence ratio is to use known flows of fuel and air and a specified chemical composition of the fuel. The mass-burning rate of the fuel must also be determined. This is possible during well-controlled laboratory experiments, but can be difficult in other situations. The phi-meter arrangement reduces the variables that must be measured to three different oxygen concentrations, and an oxygen analyser is therefore the only analysis instrument required. The phi value can be calculated according to Eq. 2, where X_{O_2} is the amount of oxygen measured when extra oxygen is added and no fuel is present, X_0 is the oxygen concentration under ambient conditions and X_m is the oxygen concentration during combustion.

$$\phi = \left(X_{O_2} - X_m\right) / \left(X_0 \cdot (1 - X_m)\right) \qquad \text{[Eq. 2]}$$

Measurements of the equivalence ratio with a mass spectrometer using the nitrogen and carbon balance

The second technique used for measuring the equivalence ratio utilises a mass spectrometer as the analysing instrument. The method is based on the fact that the ratio between the partial pressures of nitrogen and carbon dioxide can be used to calculate the phi value as in Eq. 3. The nitrogen represents the amount of air in the sample and the carbon dioxide represents the fuel.

$$\phi = \frac{p_{CO_2} / p_{N_2}}{\left(p_{CO_2} / p_{N_2}\right)_{stoich}} \qquad \text{[Eq. 3]}$$

In analogy with the phi-meter method, described above, the combustion gases are completely oxidised in a heated reactor filled with a catalyst. Extra oxygen is added to the sample stream in order to ensure that all unreacted carbon is oxidised to CO_2. The sample is continuously collected using a gas pump. The sample collection rate does not affect the mass spectrometer as long as the sample flow rate is higher than the flow through the mass spectrometer. After the reactor the sample gas is drawn through a glass orifice connected to a high-vacuum cell, which is connected to the mass spectrometer. In order to maintain a high vacuum, an Edwards's pre-vacuum pump and an oil diffusion pump are used. The vacuum created by the high-vacuum oil diffusion pump is of the order of 10^{-5} Pa. When the sample gas is let into the high-vacuum cell via the glass orifice, the pressure rises to approximately 10^{-3} Pa.

Mass spectrometer scans are made of the sample in order to detect N_2 and CO_2. Maximum points are detected for both N_2 and CO_2 together with a baseline. Subtracting the relevant baseline value for the gases from the maximum values gives the partial pressures of the two gases in the cell. Dividing the partial pressure of CO_2 by that of N_2 gives a ratio from which the phi value can be calculated. The results from these measurements are quantitative but not absolute and this simplifies the measurement procedure, as there is no need for calibration of the equipment or regulation of the flow, as long as it is held constant during the measuring period. The presence of gases other than N_2 and CO_2 does not affect the results since the relationship between the partial pressures of the studied gases is independent of additional partial pressures.

An Anavac-2 mass spectrometer (Micromass, UK) was used in these experiments. The analysis head was connected directly to the high-vacuum cell in order to analyse the gas content in real time. A data logger was used to collect the data from the mass spectrometer. An example of a mass-spectrum is given in Fig. 3.

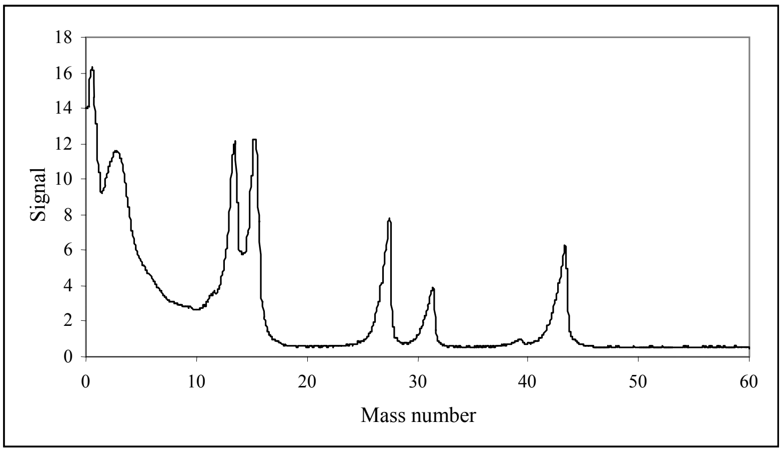

Figure 3 Mass-spectrum from a mixture of propene and air after the catalyst.

The mass spectrometer was calibrated using pure gas mixtures with different CO_2 / N_2 ratios. In Fig. 4 the phi-values for propane and propene, calculated from the different CO_2 / N_2 ratios in the gas mixtures are shown as a function of the measured CO_2 / N_2 ratio.

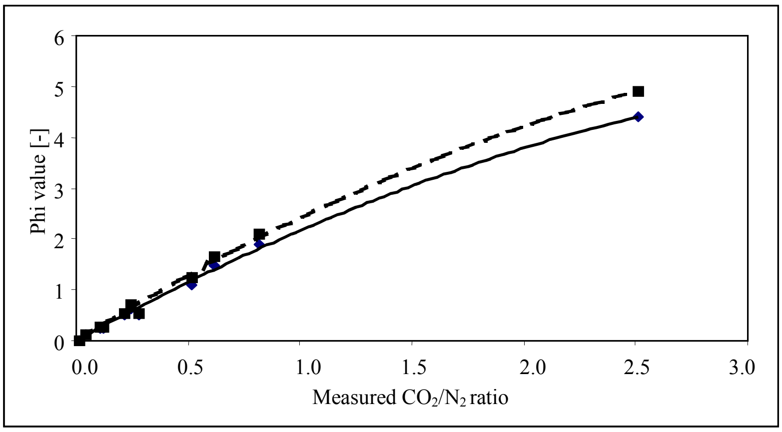

Figure 4. Phi-value as a function of the measured CO_2 / N_2 ratio. Solid line = propene, dashed line = propane.

Description of the experiments

In order to evaluate the capability of the two measuring techniques a number of experiments were performed with gaseous fuels. Propane and propene were chosen since they are readily available and they represent fuels with quite different combustion characteristics. The tests were carried out by mixing the fuel gas and air in a mixing tube and drawing a partial flow of the mixture and a known quantity of extra oxygen through a heated reactor containing a catalyst where the gas/air mixture could be fully reacted to carbon monoxide and water. The surplus fuel/air mixture was burnt at the top of the mixing tube where a propane flame was constantly burning.

In many fire situations it is desirable to be able to measure the ventilation conditions in an atmosphere where there is a high amount of unburned gases and soot. In order to investigate the versatility of the phi-meter in such situations, experiments were carried out with combustion gases. In these experiments, propene was burnt under vitiated conditions and thus a large amount of soot was produced. A sample flow from the sooty combustion gases was led into the reactor together with a surplus of oxygen. The sample gas was taken through a sampling line heated to about 200°C in order to minimise the amount of soot that collected at the inlet and inside the sampling line. The propene was burnt as a diffusion flame from a gravel-filled burner with a base diameter of 28 mm. The burner was placed at the bottom of a quartz tube, with an inner diameter of 100 mm and a height of 540 mm and the sample was withdrawn about 100 mm from the top of the tube.

RESULTS

Numerous experiments were performed in order to evaluate the performance of the phi-meter. Examples from two experiments are presented in Fig. 5. In Fig. 5a results from a propane experiment are presented. A series of three experiments with varying phi values was run and relatively good agreement was found between the measured and calculated values. There is a time delay at the beginning of the experiments due to the residence time in the reactor and in the adsorbents. This time is shorter when the system is running, as can be seen at the changeover points between different phi values. In Fig. 5b results from an experiment with propene are presented. They strongly resemble the results from the propane experiment. The peak at the beginning of the experiment is due to poor adjustment of the flow meter.

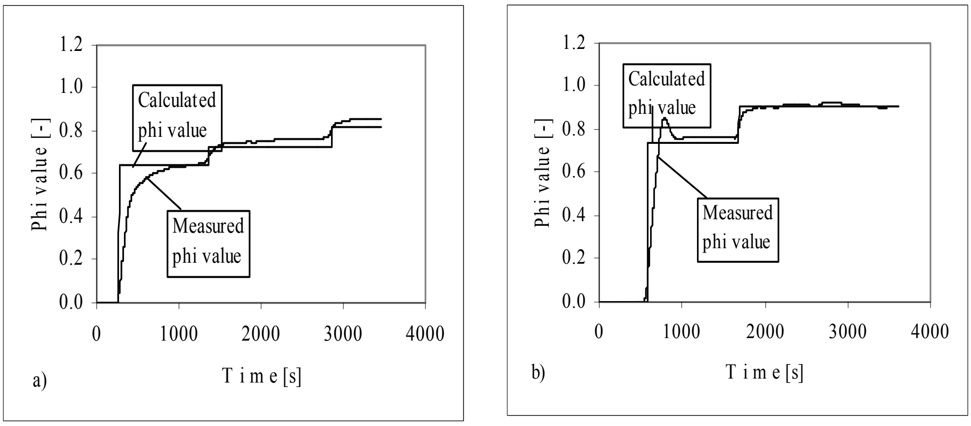

Figure 5. Measured and calculated phi values from an experiment on the combustion of a) propane and b) propene.

The results can, of course, be evaluated and presented in many ways. Comparisons between results from the phi-meter and calculated values of the GER were chosen here and are presented in Fig. 6 for gaseous fuels.

As can be seen in Fig. 6 the results from the measurements and the calculated values generally are in good agreement for fuel/air mixtures with propane and propene. The measurements with the mass spectrometer, presented in Fig. 6b, show a slightly higher tendency of this system to overestimate the phi value for propane and propene.

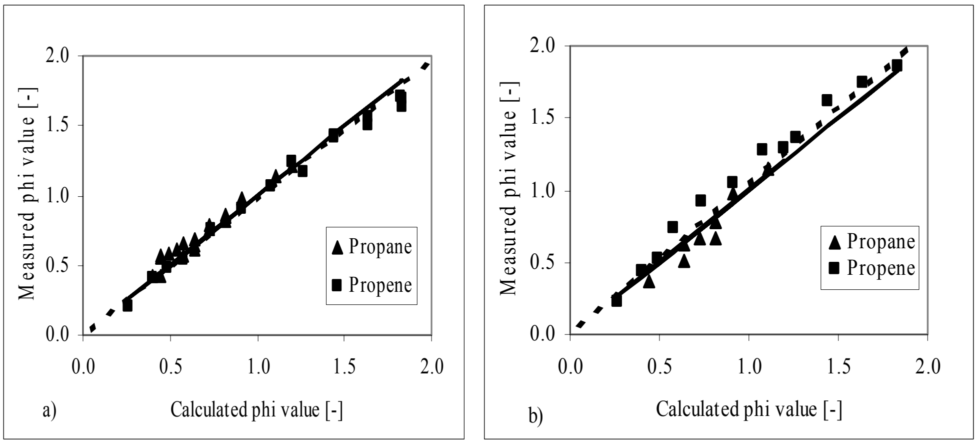

Figure 6. Measured versus calculated phi value for experiments with propane and propene. The solid straight line represents the ideal result when measured and calculated values are equal and the dotted line represents the result of a linear regression. a) Measurements using the phi-meter, the linear regression gives a constant of determination R^2=0.969. b) Measurements using the mass spectrometer, the linear regression gives a constant of determination R^2=0.957

Experiments with a propene diffusion flame were also performed and the results from the measurements with the phi-meter are presented in Fig. 7.

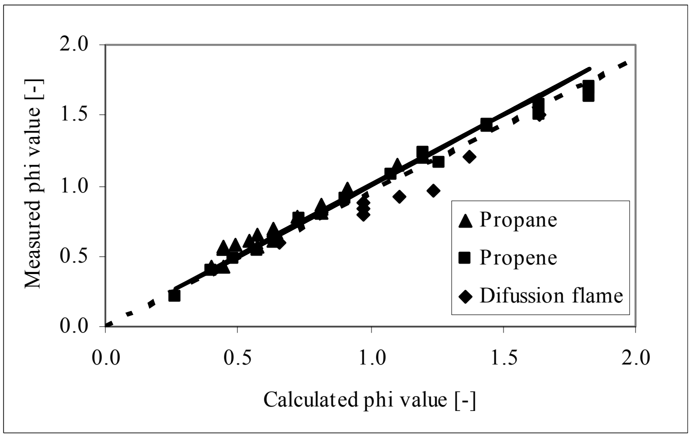

Figure 7. Measured versus calculated phi value for measurements with the phi meter. Experiments with propane, propene and a propene diffusion flame are included in the diagram. The solid straight line represents the ideal result when measured and calculated values are equal and the dotted line represents the result of a linear regression which gives a constant of determination R^2=0.950.

The ratio between the measured and the calculated phi values should ideally be 1.0. This ratio for the two methods presented is illustrated in Fig. 6 and 7. As can be seen in Fig. 7 the deviation from the calculated values are larger when the results from the experiments with the propane diffusion flame are included. The reasons for this will be discussed below.

Measurement of the global equivalence ratio in enclosure fires and in open configurations
It is sometimes of great interest to measure the equivalence ratio in enclosure fire experiments. A number of this type of experiments were performed and reported in an earlier project [10]. In order to determine the global equivalence ratio a gas sample was taken with a probe diagonally mounted across the upper part of the enclosure opening. The probe had equally spaced holes along the probe. It was assumed that the gas sample gave an average value of the gas composition in the upper part of the enclosure. The equivalence ratio measured in this way is a global equivalence ratio since it is based on the average oxygen concentration. Results from an enclosure fire experiment with heptane are presented in Fig. 8. In order to evaluate the results it is desirable to make a comparison between the measured GER and a theoretical value. The theoretical GER was based on a known mass loss of fuel, upper gas temperature in the enclosure and height of the opening of the enclosure. The expression presented as Eq. 4 was presented by Babrauskas [11] and was based on theory presented by e g Kawagoe [12].

$$\phi = \frac{\dot{m}_{fuel} \cdot \left(1 + \left(\frac{T_g}{T_a}\right)^{1/3}\right)^{3/2}}{\frac{2}{3} \cdot h^{3/2} \cdot w \cdot C_d \cdot \sqrt{2 \cdot g} \cdot \rho_0 \cdot \left(1 - \frac{T_a}{T_g}\right)^{1/2} \cdot r} \qquad \text{[Eq. 4]}$$

Where $\dot{m}_{fuel}$ is the mass loss of fuel, T_g is the upper gas temperature in the enclosure, T_a is the ambient temperature, h is the opening height, w is the opening width, C_d is the discharge coefficient for the opening (set to 0.68) [13], ρ_0 is the density of the surrounding air and r is the stoichiometric fuel/air mass ratio. The time difference between the two curves in Fig. 8 is due to the time constant of the measuring system.

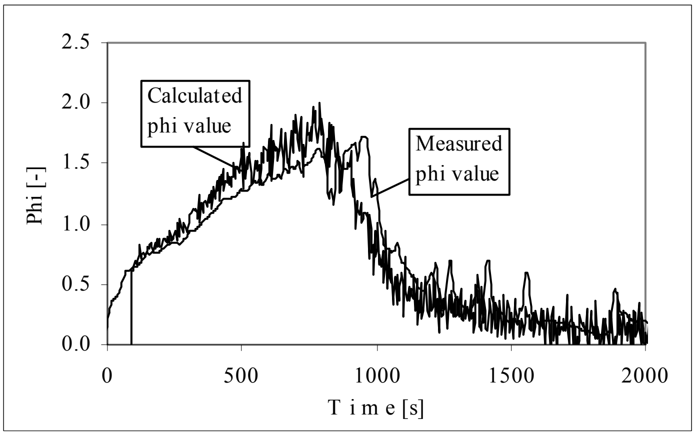

Figure 8. Comparison between theoretical phi value and GER measured with the phi-meter for a heptane pool fire in an enclosure.

DISCUSSION AND CONCLUSIONS

The ventilation conditions during combustion or during a fire constitute an important variable, which governs the production of combustion gases such as CO and CO_2. In order to find a useful way of determining the equivalence ratio the phi-meter concept presented in [1] was evaluated and compared with a technique using mass spectrometer analysis.

The two methods have some features in common as regards their suitability for measuring the equivalence ratio in different situations and experimental set-ups. Both methods can be used to measure the GER as well as the local equivalence ratio. The probe size can, however, be much smaller when the mass spectrometer approach is used, thus making it possible to measure spatially very small differences in composition of the combustion gases. The probe in this case can have a diameter less than 1 mm while for the phi-meter the probe diameter is of the order of 3-8 mm.

Absorption media for H_2O and CO_2 are an important component in the phi-meter concept since the whole technique is based on the assumption that measurements can be made on pure O_2 and N_2. These absorption media can, however, cause some problems since Ascarite and NaOH are prone to clogging when a large amount of CO_2 has been absorbed. It is vital that the absorbents are fresh when a new measurement is started. The amount of absorbent is, of course, also a matter of interest since larger amounts of absorbents take longer to clog, but the time constant of the system also increases which is undesirable. Clogging is not a problem with the H_2O absorbent.

The sample flow required for analysis also differs for the two methods. The flow necessary for the phi-meter is governed by the demand of the oxygen meter, and in this case a flow of $8 \cdot 10^{-6} m^3/s$ was used. The flow for the mass spectrometer is less than $10^{-9} m^3/s$ at atmospheric pressure.

The experimental results presented are in relatively good agreement with the theoretically calculated values for propane and propene. Some of the discrepancies may be due to the accuracy of the flow meters for fuel and air. These were ordinary glass-tube variable-area flow meters from Fischer & Porter and especially at the low flow end of the scale the accuracy is not very good.

In order to identify possible reasons for the discrepancies between the measured and calculated phi values for the propene diffusion flame a number of tests were performed in which soot was collected on filters at the inlet and outlet of the reactor. Experiments were made with reactor temperatures from 300°C to 800°C in order to study the influence of the reactor temperature. All these experiments were performed with the Pt-catalyst. The results from this exercise are presented in Fig. 9. It was found that the reactor temperature seemed to have no effect on the efficiency of the combustion of the soot.

About 10% of the soot entering the reactor is not combusted. The reasons for this are not fully understood but some suggestions can be made. The combustion gases are introduced at one end of the reactor through a 6 mm sampling line into the 30 mm wide reactor filled with catalyst. If the sooty combustion gases are cooler than the reactor they will lower the temperature at the inlet side of the reactor thus causing a conglomerate of soot particles there, which will not be as easily combusted as the rest of the sample gas. This soot at the inlet might hinder the rest of the soot from being evenly distributed throughout the catalyst and the soot will therefore take the easiest way through the reactor and complete combustion will not be achieved.

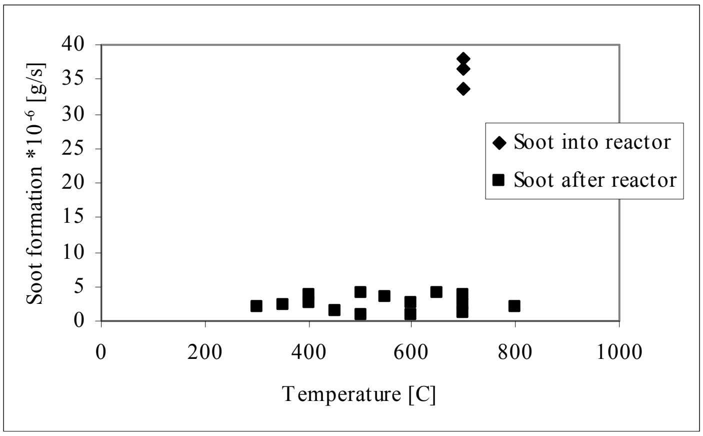

Figure 9. Soot from the propene diffusion flame collected on filters at the entrance to the reactor and after the reactor.

In calculating the theoretical phi value the assumption was made that everything that entered the reactor was combusted to CO_2 and H_2O. In the case of the propene diffusion flame it was found that this was not the case, since small amounts of soot was collected after the reactor. According to the SFPE [14] under well-ventilated conditions about 10% of the mass burnt are in the form of soot and at equivalence ratios around 2 some 20% is converted to soot. This was taken into account when presenting calculated phi values for the propane diffusion flame experiments in Fig. 7.

There is a need for a versatile method that can be used to measure the local or global equivalence ratio during a fire or in combustion experiments. The two methods presented above are possible candidates in situations where global and local equivalence ratios need to be measured. In its present conformation, the phi-meter gives more consistent results than the mass spectrometer approach but the latter can be considerably improved by using a mass spectrometer with better resolution. The primary disadvantages of the phi-meter are the need for fresh adsorbents. Of course, large amounts of adsorbents can be included, but this increases the time constant of the system, which is undesirable.

In order to improve the phi-meter a more thorough investigation of the performance of the catalyst should be made so that the amount and the working temperature of the catalyst can be optimised. The sample lines could also be made shorter, thus improving the time constant. The problem associated with the accuracy of the flow meters can, of course, also be solved but this is a minor problem since it is proposed that the phi meter be used primarily in experiments where the complete flow of combustion gases is measured with one flow meter, and thus the small flows encountered during calibration will not be employed.

It can be concluded that both methods are possible candidates for measurement of the equivalence ratio in a fire and in combustion experiments, but more work is needed in order to develop a method that is reliable and easy to include in a measuring system.

REFERENCES

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1 Babrauskas, V., Parker, W. J,. Mullholland, G. and Twilley, W. H., "The phi meter: A simple, fuel-independent instrument for monitoring combustion equivalence ratio.", *Rev. Sci. Instrum.* Vol 65, No. 7: 2367-2375 (1994).

2 Pitts, W. P., "The Global Equivalence Ratio Concept and the Prediction of Carbon Monoxide Formation in Enclosure Fires", National Institute of Standards and Technology Monograph 179, Gaithersburg, MD, 1994, 171 p.

3 Neij, H., Thesis "Fluorescence for Precombustion Diagnostics in Spark-Ignition Engines", ISRN LUTFD"/TFCP-41-SE, 1998.

4 Andersson, Ö., Thesis "Development and application of Laser Techniques for Studying Fuel Dynamics and NO Formation in Engines", ISRN LUTFD"/TFCP-61-SE, 2000.

5 Gottuk, D. T., "Generation of carbon monoxide in compartment fires", National Institute of Standards and Technology NIST-GCR-92-619, , December 1992, 265 p.

6 Beyler, C. L., "Major Species Production by Diffusion Flames in a Two-layer Compartment Fire Environment", *Fire Safety Journal* Vol. 10, No. 1, 47-56 (1986).

7 Thornton, W. M., "The Relation of Oxygen to the Heat of Combustion of Organic Compounds", *Philosophical Magazine and Journal of Science*, Vol.33, No. 196: 196-203 (1917).

8 Parker, W. J., "Calculations of the Heat Release Rate by Oxygen Consumption for Various Applications", National Bureau of Standards NBSIR 81-2427-1, Center for Fire Research Washington, DC 20234, March 1982, 41p.

9 *"Heat Release in Fires"*, edited by Babrauskas, V and Grayson, S. J., Elsevier Applied Science, London, Chapter 3, p. 31-59, 1992.

10 Anderson, B., Babrauskas, V., Holmstedt, G. Särdqvist, S., Winter, G., *"Simulated fires in substances of pesticide type"*, Department of Fire Safety Engineering, Lund University, Report No. 3087, 1999, 95 p.

11 Babrauskas, V., Thesis "Fire Endurance in Buildings", Report No. UCB FRG 76-16, Fire Research Group, University of California, Berkeley, U.S., November 1976.

12 Kawagoe, K., "Fire Behaviour in Rooms", Report of the Building Research Institute of Japan, No. 27, September 1958, 73 p.

13 Prahl, J. and Emmons, H. W., Fire Induced Flow through an opening", Technical report No 12, 1975, 41 p.

14 Tewarson, A., *"Generation of Heat and Chemical Compounds in Fires"*, Section 3, Chapter 4 in The SFPE Handbook of Fire Protection Engineering, 2nd ed, NFPA publication number:HFPE-95, National Fire Protection Association, 1995.

Simulated Fires in Substances of Pesticide Type

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Simulated fire, medium scale fire experiment, combustion gases, combustion products, phi value, chemicals, polymers, ventilation condition.

Abstract

In order to characterise fires in chemical warehouses, 38 medium scale experiments have been conducted. The experiments were performed in a 0.66m^3 combustion chamber. On-line measurements were made of combustion gases (CO_2, CO, HC and NO_x), mass loss, smoke, temperatures, external radiation and phi-values. Intermittently gas and soot samples were collected and analysed for content of organic compounds and amount of soot produced. Main variables during the experiments were external radiation, fire diameter, opening configuration and ventilation condition. The medium scale was chosen in order to give a test method which is more convenient to work with, less expensive than full-scale experiments and still rather well simulates the conditions in a real fire.

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Summary

During the 20th century a number of disastrous fires in warehouses storing chemicals, and in chemical production plants have occurred. This has increased the awareness of the problems connected with storing large amounts of chemicals. As a result of this, new legislation and guidelines have been implemented through out Europe. One part of this is the SEVESO directive, which was introduced in Europe during 1987. Currently the SEVESO II directive is being introduced. A lack of knowledge was found concerning substances produced in fires involving chemical substances, especially organic substances containing heteroatoms, like nitrogen, sulphur, phosphorus and chlorine.

The project TOXFIRE [1], a part of the CEC ENVIRONMENT programme, has as its main objective to develop a basis for two sets of guidelines in relation to fires in chemical warehouses. These are guidelines for the fire safety engineers to be used in accident prevention [2] and guidelines for the fire brigade to be used if an accident occurs [3]. The guidelines will be the outcome of a detailed and systematic study of chemical fires supplemented by experiments based on model compounds to determine important properties of the substances involved and the source characteristics and assessment of other parameters of importance for fire scenarios.

In this report results from experiments in a medium scale combustion chamber are presented. The chamber was $0.66 m^3$ and the amount of substance burned was between 0.3kg and 2.3kg. The walls and the ceiling of the combustion chamber can be heated electrically in order to apply external radiation. Experiments were carried out using a number of chemical substances of different nature as fuel. The tested substances were: chlorobenzene, dimethoate, heptane, nylon-6,6, tetramethylthiuram monosulfide (TMTM) and 4-chloro-3-nitrobenzoic acid (CNBA). During the experiments online measurements in the exhaust duct were made of combustion gases such as CO, CO_2, NO_x, O_2 and unburned hydrocarbons. Results from the gas analysis are presented as yields in g component produced per g substance burned. Yields are given for CO, CO_2, NO_x, HC and soot. Grab samples were taken intermittently and analysed by GC-MS with respect to content of organic combustion products. A qualitative analysis of organic substances found in the GC-MS analysis is presented. A large number of substances were detected, including varying amounts of the original substance being burned. The rate of heat released, RHR, during the experiments was measured using the oxygen consumption technique. The RHR ranged from 0.4kW to 47kW. Continuous measurements were also made of temperatures inside the combustion chamber, in the opening of the chamber and in the exhaust duct. Radiation inside the chamber and mass loss was also monitored continuously.

In all 38 experiments were conducted. The conditions during the experiments varied with respect to the degree of ventilation, measured as the phi-value. Phi-values ranging from 0.04 to 1.4 were detected. It was found impossible to achieve higher phi-values in the experimental set-up used here. The ventilation was varied by changing the opening height. The results indicate that the phi-value is a useful parameter when it comes to characterisation of enclosure fires. The opening width was kept constant at 0.45m in all experiments. A comparison between the measured and calculated phi-values show that these are in good agreement. Since some of the substances contain heteroatoms like chlorine and phosphorus they are difficult to

ignite, in fact these elements are used in fire retardant applications. Thus it was necessary to apply external radiation in some of the experiments in order to achieve sustained burning of the tested substance.

Contents

Nomenclature

A	Area of the exhaust duct [m^2]
C_d	Discharge coefficient [-]
h	Height of opening [m]
g	Gravitational constant [m/s^2]
$\Delta H_{C,ox}$	Heat release per unit mass oxygen consumed [kJ/gO_2]
ΔH_T	Theoretical heat of combustion [kJ/g]
I	Light intensity during the test [-]
I_0	Light intensity without smoke [-]
K	Extinction coefficient [1/m]
L	Light beam length through the smoke [m]
m	Mass concentration of the smoke aerosol [g/m^3]
m_{fuel}	Total mass of sample burned [g]
m_i	Total mass of gas *i* produced [g]
m_{soot}	Amount of soot [g]
$\dot{m}_{fuel}$	Amount of fuel burned [g/s]
$\dot{m}_{O_2}$	Amount of oxygen consumed [g/s]
M_C	Molecular weight of carbon [g/mole]
M_{CO}	Molecular weight of CO [g/mole]
M_{CO_2}	Molecular weight of CO_2 [g/mole]
M_{NO_2}	Molecular weight of NO_2 [g/mole]
M_{nylon}	Molecular weight of nylon [g/mole]
Δp	Pressure difference in the exhaust duct [Pa]
q	Rate of heat release [kW]
r	Stoichiometric fuel/air mass ratio [-]
T_0	Temperature of ambient air [K]
T_e	Temperature in the exhaust duct [K]
T_u	Mean temperature in the hot upper layer in the combustion chamber [K]
$\dot{V}$	Volume flow in the exhaust duct [m^3/s]
w	Width of opening [m]
X_0	Concentration of oxygen in the surrounding air [-]
X_i	Mole fraction of gas *i* in the exhaust duct [-]
X_m	Scale value on the oxygen meter [-]
X_{O_2}	Molar fraction of oxygen in the oxygen meter with extra oxygen [-]
$X_{O_2}^0$	Mole fraction of O_2 in the incoming air [-]
Y_i	Yield of product *i* [g/g]
α	Expansion factor [-]
ϕ	Equivalence ratio [-]
ρ_0	Density of air at ambient temperature [kg/m^3]

σ_m	Extinction area [m^2/g]
Ψ_C	Yield of C [g/g]
Ψ_{CO}	Yield of CO [g/g]
Ψ_{CO_2}	Yield of CO_2 [g/g]
Ψ_{NO_2}	Yield of NO_2 [g/g]

1 Introduction

This report constitutes a part of the CEC ENVIRONMENT project entitled ”TOXFIRE - Guidelines for Management of Fires in Chemical Warehouses”[1].

The objective of the project is to develop a basis for two sets of guidelines in relation to fires in chemical warehouses; guidelines for the fire safety engineers to be used in accident prevention [2], and guidelines for the fire brigade to be used if an accident nevertheless occurs [3]. The guidelines will be the outcome of a detailed and systematic study of chemical fires supplemented by experiments based on model compounds to determine important properties of the substances involved and the source characteristics and assessment of other parameters of importance for fire scenarios. In addition, the consequences to humans and the environment of the fire will be included. A common introduction and approach to the guideline documents is presented in [4].

Based on a number of parameters the substances will be classified. The classification of substances requires studies and experiments of ignitability, heat release, burning rate, smoke evolution, combustion products and influence on the combustion products of the packaging materials. The characterisation of the source will use parameters obtained by carrying out combustion experiments of various scales and by studying the effects of scaling. In addition, the fire scenarios will be characterised by the degree of ventilation, the packaging materials, the stacking of the materials and the response of the building. In addition, the suppression is an important parameter, i.e. active and passive suppression and the fire brigade tactics. The consequences to humans as well as the environment will be assessed. Finally, existing modelling methods used for risk assessment will be studied, along with the handling and prevention of accidents. These investigations will lead to the development of the basis for guidelines document for the fire safety engineers and the fire brigades. In parallel also a quick decision system to be used by the fire chief in case of a chemical fire will be developed.

The project comprises the following workpackages:

- WP 1: Screening of substances and micro scale experiment
- WP 2: Small scale cone calorimeter experiments
- **WP 3: Medium scale (model scale) experiments**
- WP 4: Indoor large scale underventilated fire tests
- WP 5: Effects of storage configuration and fire spread models
- WP 6: Sampling and analysis of dioxins
- WP 7: Consequence models for health hazards
- WP 8: Consequence models for ecotoxicological effects
- WP 9: Quick decision system
- WP10: Guidelines for safety engineers
- WP11: Guidelines for fire brigades
- WP12: Project management

The participants in the project are:

- Risø National Laboratory, Denmark
- South Bank University, UK
- VTT - The Technical Research Centre of Finland
- **Lund University, Sweden**
- SP - The Swedish National Testing and Research Institute
- DMU - The Danish National Environmental Research Institute

This report contains the results and conclusions from WP 3: Medium scale experiments.

2 Experimental method

The medium-scale combustion tests were performed in a 0.66m^3, combustion chamber. The amount of substance burned was between 0.3kg and 2.3kg. The combustion chamber is equipped with a hood to collect all smoke and combustion gases. The hood is connected to an exhaust duct where on-line measurements were made. A phi-meter was incorporated into the measuring system to determine the degree of ventilation during the experiments. Gas samples and soot samples were collected intermittently. The gas samples were analysed with gas chromatography-mass spectrometry and with ion chromatography. Soot was collected intermittently on a filter in order to determine the mass of soot produced.

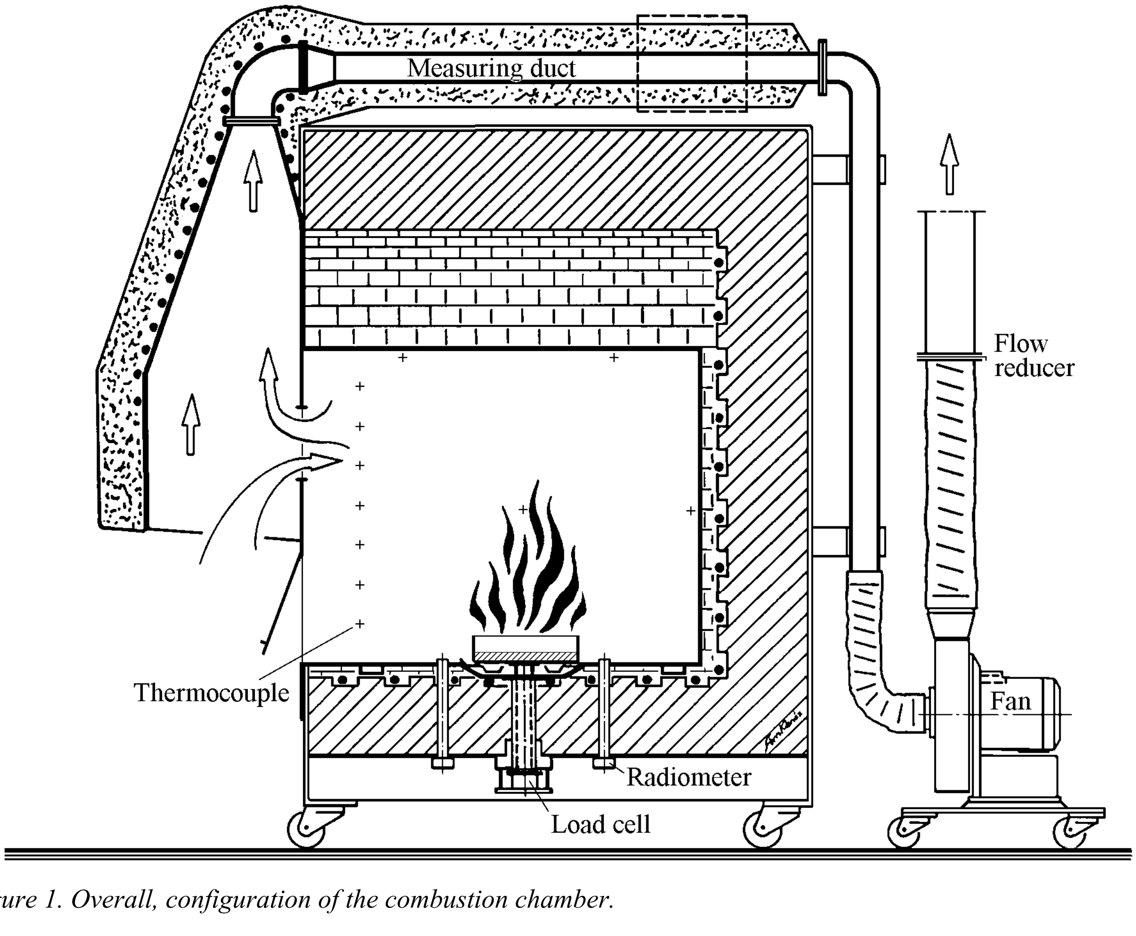


Figure 1. Overall, configuration of the combustion chamber.

2.1 The combustion chamber

The stainless steel combustion chamber used during these experiments is fitted inside a furnace constructed of ceramic, high temperature bricks. The internal dimensions of the steel chamber are 0.75m (width), 1.10m (depth) and 0.80m (height), giving a volume of 0.66m^3. This is approximately 1/3 of the standard, ISO room corner test (ISO 9705). The internal dimensions of the oven are 0.80m (width), 1.10m (depth) and 1.09m (height). This gives a portion of air above the steel chamber and between the sidewalls of the chamber and the oven sidewalls. There is an opening in one wall. The opening width is 0.45m. The height of the opening is adjustable in order to change the ventilation conditions. Stainless steel covers were used to change the opening height. The walls and ceiling in the combustion chamber can be electrically heated in order to apply external radiation. The maximum temperature achievable in the chamber corresponds to a radiation towards the floor of approximately 50kW/m^2. The over all configuration of the combustion chamber is given in figure 1.

2.2 On line measurements inside the combustion chamber

A number of measurements were made inside the combustion chamber. A load cell was positioned in the centre of the floor beneath the chamber. The exact position can be seen in figure 1. The load cell was connected to a platform inside the chamber via a ceramic rod. This arrangement was made to avoid thermal influence on the load cell as much as possible. Thus, the tested substances are placed 0.05m above the bottom of the combustion chamber. Two radiometers were mounted in the floor of the combustion chamber. They were of the Gunners' type [5], and were positioned in front and behind the weight-measuring device. The exact positions of the radiometers were 0.43m from the opening and 0.20m from the rear wall. Both radiometers were positioned along the centre line of the chamber. The upper surfaces of the radiometers were 10mm above the bottom of the combustion chamber. The radiometers were calibrated in a spherical furnace according to the procedure described in [6]. An array of eight thermocouples was mounted vertically in one corner of the chamber, 0.05m from the adjacent walls. The thermocouples were mounted at the following distances from the ceiling: 5mm, 10mm, 15mm, 20mm, 30mm, 40mm, 50mm and 60mm. Three thermocouples were placed on the walls; each of these was mounted in the centre of the wall and three in the ceiling to measure surface temperatures. The thermocouples in the ceiling were mounted according to the following specification: One thermocouple was placed 0.30 m from the opening wall and 0.15m from the right-hand wall and two thermocouples were placed 0.30m from the rear wall and 0.15m from the right-hand wall and from the left-hand wall respectively. Specifications on the measuring equipment are presented in table 1.

Table 1. Measuring equipment used inside the combustion chamber.

Measurement	**Equipment**	**Range**	**Accuracy**
Radiation	Gunners' radiometers	0 - 100kW/m^2	± 5%
Mass	Load cell	0 - 10kg	± 1g
Temperature	Thermocouple Chromel Alumel, d=0.25 mm	0 - 1300°C	0.4%

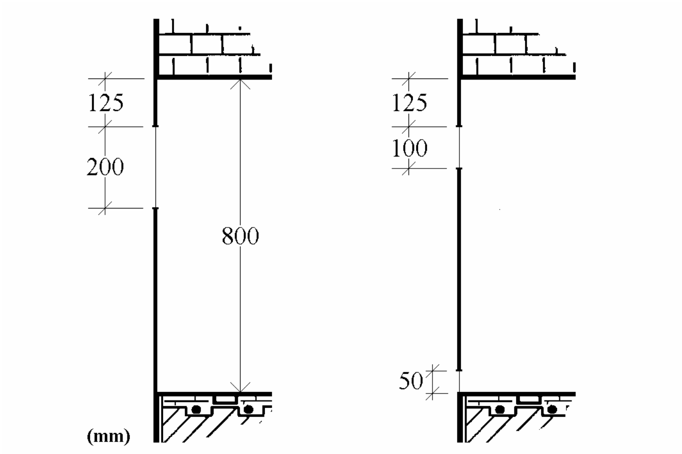


Figure 2. Opening configurations used in the combustion chamber. The left one was used in test 001-021 and the right was used in test 022-038

2.3 Measurements in the opening

The opening of the chamber had a width of 0.45m in all experiments. The height of the opening however was varied in order to change the ventilation conditions. This was achieved by placing stainless steel covers of different size in the opening. The design of the opening is presented in figure 2. In the centre of the opening an array of seven thermocouples was mounted in order to measure the gas temperature of the hot combustion gases and the air entering the chamber. The thermocouples were evenly distributed along the vertical centreline of the opening. See figure 3 for position of the thermocouples. Two probes were mounted in the opening for taking gas samples to the phi-meter and for gas analysis. Each of these probes had three 1.5mm holes. The positions of these holes are indicated with small arrows in figure 3. The gas samples were drawn to the phi-meter and in some tests, concentrations of CO, CO_2 and O_2 in the opening were measured. The probes were mounted diagonally in the upper part of the opening to ensure that the samples were taken in the hot gases leaving the chamber. The concentrations are a mean value of the concentrations in the hot upper layer in the chamber. The probes are made with three holes equally spaced along the probe. The phi probe was mounted with the holes facing the inside of the chamber in order to get samples containing all types of combustion products, including soot. The probe for gas sampling on the other hand was mounted with the holes facing the outside in order to avoid soot in the samples. The positions of the probes are given in figure 3.

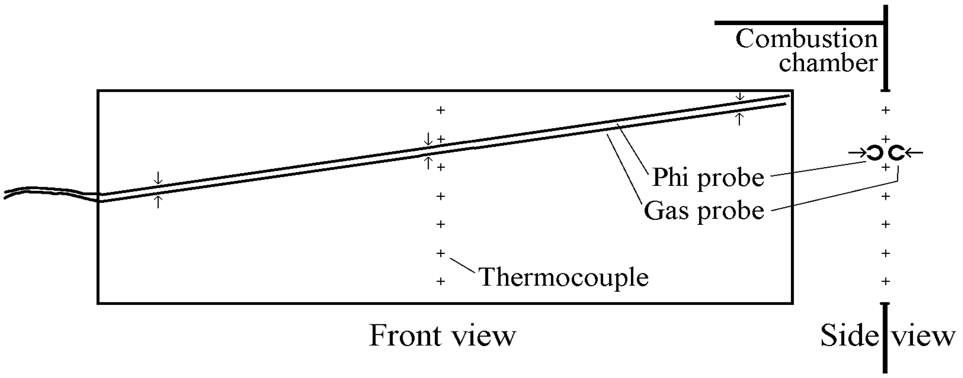


Figure 3. Positions of thermocouples and gas probes in the opening of the combustion chamber.

When studying fires with varying degrees of ventilation a parameter phi, the combustion equivalence ratio has been introduced to describe the ventilation condition [7]. Equipment by which this parameter can be measured has been used in these experiments. The main principle for the phi-meter is to expose the combustion gases to a catalytic combustion in a reactor with a platinum wire catalyst. In the original layout for the phi-meter, the temperature in the reactor was 1000°C. A change of the catalyst, to a platinum catalyst in pellet form, made it possible to reduce the reactor temperature to 400ºC. In the reactor, all combustion products are transformed to CO_2 and H_2O. Following the reactor, the gases go through a train of filters where CO_2 and H_2O are removed. The dry remaining nitrogen-oxygen mixture is then analysed with respect to oxygen content. In order to cover fuel rich conditions a known amount of pure oxygen is introduced to the reactor. An overall view of the phi-meter is given in figure 4. The conditions of the phi-measurements were the same throughout the experimental series. The total mass flow through the system was $0.6 \cdot 10^{-3} m^3$/min, the flow of pure oxygen was $0.13 \cdot 10^{-3} m^3$/min and the temperature in the reactor was 400°C.

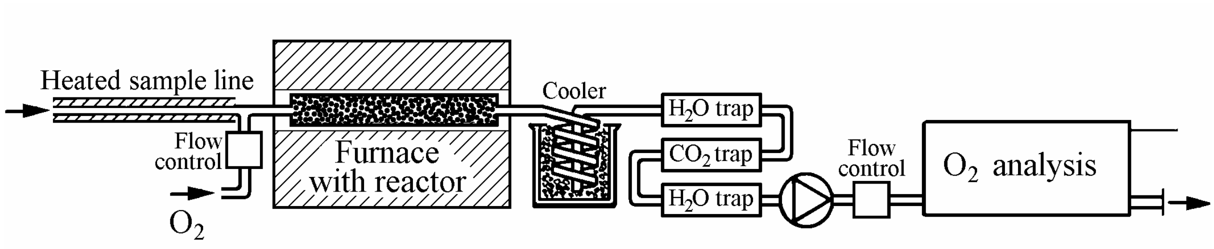


Figure 4. Overall view of the phi-meter.

Much effort has been put into calibrating and verifying the function of the phi-meter. In figure 5 a calibration diagram for the phi-meter is presented. The calibration was performed with propane. The time constant for the phi-meter was measured to 30 s. The phi-meter is sensitive to the amount of oxygen added to the system. This means that by changing the added amount of oxygen, the working range for the phi-meter is also changed. When a certain level of phi is anticipated the oxygen level should be chosen accordingly to suit this measuring range.

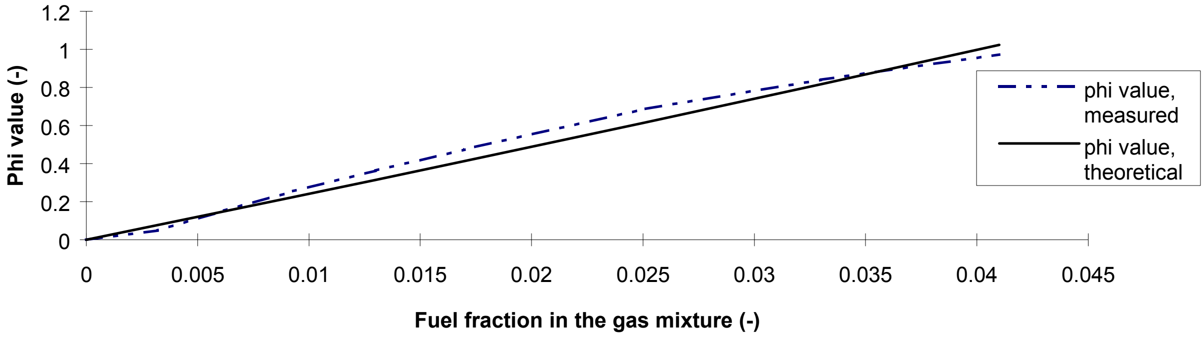


Figure 5. Calibration curve for the phi-meter showing a comparison between theoretical and measured phi values.

2.4 On line measurements in the exhaust duct

A hood, which collects all smoke and combustion gases from the combustion chamber, is located outside the opening. The hood is connected to an exhaust duct, including a flow stabilising section, where all sampling probes are located. The whole system is thermally insulated to avoid condensation problems. A 2.2kW radial fan exhausts the smoke. The flow in the duct can be regulated by means of introducing flow reducers of varying size.

The exhaust duct is equipped with a bi-directional pitot tube, a thermocouple, a light absorption measuring device and a probe for continuous measurements of concentrations of O_2, CO_2, CO, NO_x and HC (unburned hydrocarbons). Specifications for the measuring equipment are presented in tables 2 and 3. The overall layouts are given in figure 6.

Table 2. Measuring equipment used in the exhaust duct.

Measurement	**Equipment**	**Range**	**Accuracy**
Smoke	Lamp with colour temperature 2900 ± 100K And photo cell detector	0 - 100%	Lamp: ±0.2% Detector: Linear within 5%
Pressure drop	Pressure transducer connected to a Bi-directional pitot tube	0 - 400Pa	± 0.5%
Temperature	Thermocouple, Chromel Alumel, D= 0.25mm	0 - 1300°C	± 0.4%

Table 3. Gas analysis equipment for continuos analysis in the exhaust duct.

Measurement	Equipment	Range, accuracy	Calibration gas
O_2	Siemens Oxymat 5E Paramagnetic	10-21vol% ± 1% of full scale	21% 9.94 ± 0.200%
CO	Siemens Ultramat 22P, Non-dispersive IR-absorption	0-1vol% ± 1% of full scale	0.202 ± 0.0040ppm 202 ± 4.04ppm
CO_2	Siemens Ultramat 22P, Non-dispersive IR-absorption	0-20vol% ± 1% of full scale	4.99 ± 0.0998% 0.502 ± 0.010%
NO_x	Analysis Automation Limited, Chemiluminiscens analysis, model 443	0-100ppm ±1% of full scale	93.6 ± 1.9ppm
HC	Siemens Fidamat K FID (flame ionisation detector)	0-100ppm ± 1% of full scale	50.9 ± 1.0ppm propane

The mass flow in the exhaust duct was calculated according to NT FIRE 025 [8], using the values from the pitot tube and the thermocouple in the duct. The smoke extinction was also measured according to NT FIRE 025. The gas samples for continuos measurement of O_2, CO and CO_2 were cooled and dried and freed from particles before they entered the analysis instruments. The samples for NO_x and HC measurements were taken through a sampling line heated to 200°C and a heated smoke filter. The gas analysis equipment was calibrated with zero and span gases of concentrations within the same area of magnitude as the expected test samples. All measurements were performed on-line and a Schlumberg data-logger was used to collect the data and transfer them to a PC. The scan interval was 5s.

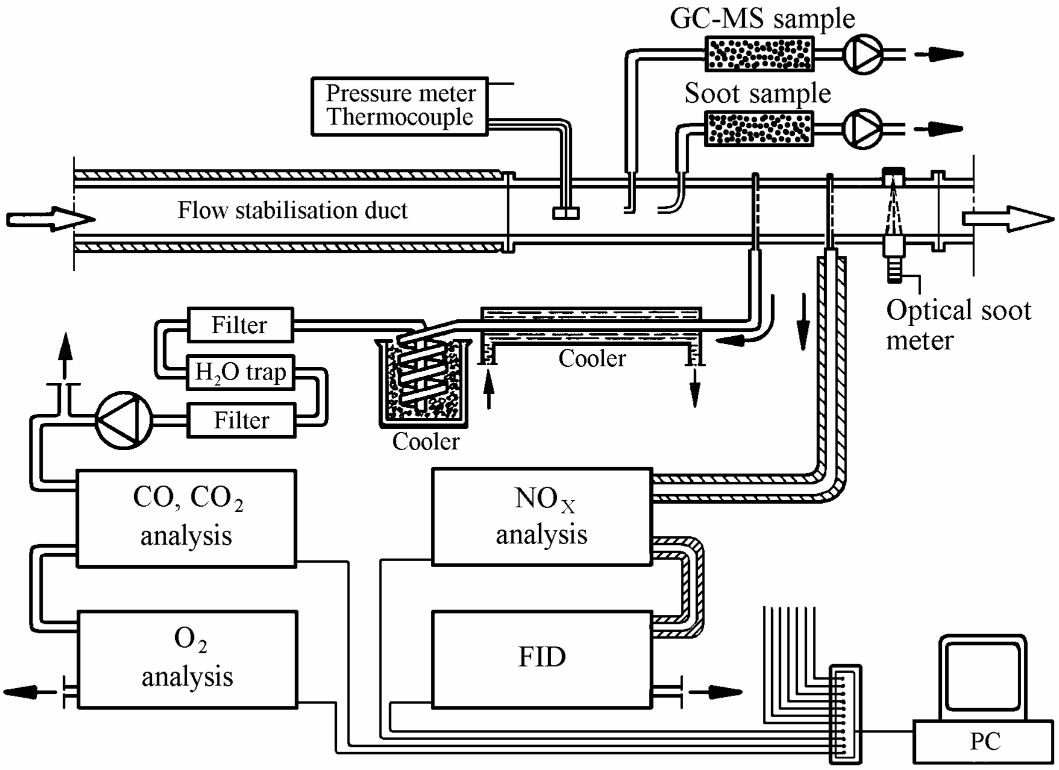


Figure 6. Layout of the measuring equipment for the on line measurements in the exhaust duct.

2.5 Intermittent gas samples

Gas samples were taken intermittently from the exhaust duct in order to determine the main components in the combustion gases. The samples were drawn iso-kinetically from the sample probe at intervals during which the combustion was deemed approximately constant. The sampling period was typically 5 minutes. The combustion products were adsorbed on Amberlite XAD-2 and on activated carbon. XAD-2 is a frequently used adsorbent for sampling of gaseous components. An extra XAD-2 tube was mounted directly after the first one to take care of any excess products. The first tube was filled with 600 mg XAD-2 and the second tube with 300 mg. After the XAD-2 tubes were two tubes with activated carbon in order to collect the substances that are not adsorbed on the XAD-2. The combustion gases collected on XAD-2 were extracted with diethyl ether and the products adsorbed on carbon were extracted with carbon disulphide. The extracts were subsequently analysed with GC-MSD and GC-MSD-FID. The column in the MSD was a non-polar column.

The identification of the substances in the combustion gases was made with the GC-MSD and subsequently a quantitative analysis was made with FID when this was feasible. Analysis was also made of the content of anions in the combustion gases. This was achieved by letting the gas flow through a train of two impinger bottles with a water solution of NaOH with pH9. Analyses were made of Cl^- and SO^{2-} content when this was relevant. These analyses were made with ion chromatography.

Gas samples were also taken in order to study the soot content in the combustion gases. The soot particles were collected on filters that were dried and weighed before test and after test to determine the amount of soot produced during the test. The soot filters were made of Teflon and were of the type Millex-FG_{50} from Millipore. The optical measurements in the duct were transformed to yields and together with the amount of soot collected on the filter, this gave the smoke extinction area for the burned substance. This was done according to the principles described in section 3.5.

2.6 Selection and properties of tested substances

As mentioned earlier the TOXFIRE project comprises a number of different work packages. In WP1 to WP4, substances were tested in different scales and thus varying amounts of substances were tested. Depending on the tested amount the number of substances that could be tested varied between the testing methods. Different criteria had to be met in different testing situations. The largest number of tested substances could be dealt with in the small-scale tests. In the medium scale tests six substances were tested. The tested substances are presented in table 4.

Table 4. Materials tested

Substance	**State, form**
Heptane, C_7H_{16}	Liquid
Chlorobenzene, C_6H_5Cl	Liquid
Tetramethylthiuram monosulfide, TMTM, $C_6H_{12}N_2S_3$	Extrusion granules
4-Chloro-3-nitrobenzoic acid, CNBA, $C_7H_4ClNO_4$	Powder
O,O-dimethyl-S-(N-methylcarbamoylmethyl)-Phosphorodithioate, Dimethoate, $C_5H_{12}NO_3PS_2$	Formulation with cyclohexanon and xylene
Nylon-6,6, $C_{12}H_{22}N_2O_2$	Solid polymer, pellets

The materials in table 4 were chosen from the list of materials common to the TOXFIRE project. They represent a number of different types of substances. Heptane is a simple hydrocarbon fuel, chlorobenzene is a chlorinated solvent, TMTM represents substances containing sulphur, CNBA contains chlorine and nitrogen, Dimethoate is a pesticide containing nitrogen, phosphor and sulphur and nylon-6,6 is a polymer which has been used as a reference material throughout the STEP [9] and the TOXFIRE projects. The selection of substances was made to give a wide spectrum of types of substances as regards content of heteroatoms such as chlorine, nitrogen, phosphorus and sulphur. It was also required that the substances have controllable combustion behaviour and they could not be so highly toxic that the staff or nearby persons would be endangered.

The tested substances represent a wide spectrum as regards their burning behaviour. The chlorine containing substances are inherently fire retardant and thus rather difficult to ignite. Nylon 6,6 is a thermoplastic polymer and melts before it is possible to ignite the substance. Nylon 6,6 therefore needs external heat flux in order to ignite. CNBA was also found hard to ignite. In some of the tests polypropylene was added and acted as an ignition source. Selected properties of the tested substances are given in table 5.

Table 5. Molecular weight, theoretical heat of combustion and theoretical yields for the tested substances.

Substance	M_w [g/mole]	$\Delta H_{C,ox}$ [kJ/gO$_2$]	ΔH_T [kJ/g]	Ψ_C [g/g]	Ψ_{CO2} [g/g]	Ψ_{CO} [g/g]	Ψ_{NO2} [g/g]	Ψ_{HCl} [g/g]	Ψ_{SO2} [g/g]
Heptane	100.2	13.1	44.59	0.84	3.08	1.96	-	-	-
Chlorobenzene	112.6	13.16	26.19	0.64	3.66	1.49	-	0.325	-
TMTM	208.4	13.96	25.73	0.35	1.28	0.82	0.442	-	0.922
CNBA	201.6	14.96	13.66	0.42	1.54	0.98	0.228	0.181	-
Dimethoate*	152.6	13.1	42.76	0.46	3.66	1.03	0.301	-	0.327
Nylon-6,6	226.4	12.38	28.94	0.64	2.35	1.49	0.407	-	-

** Dimethoate was tested as a formulation consisting of 41% Dimethoate, 45% cyclohexanon and 14% xylene. The figures in the table refer to the formulation.*

2.7 Experiments

The performance of each experiment followed a standard procedure. The measuring equipment was calibrated prior to start of the experiment. After the calibration the data logger was started. The substance was placed in a cylindrical container on the load cell, in the centre of the combustion chamber. Containers having an inner diameter from 0.10m to 0.40m were used. The tested substance was in most experiments ignited with a small flame. For some substances, more intense ignition sources were necessary. The sample was left to burn until self-extinction in most experiments. In a few experiments, extinction with CO_2 was necessary due to uncontrolled burning.

Apart from the variation in size of the sample, the ventilation and the external radiation to the sample was varied. The ventilation was changed by altering the height of the opening to the combustion chamber. The largest ventilation was with an opening of 0.2m, at the top of the chamber. For the other ventilation conditions, the opening at the top was 0.1m and in addition, a small opening was arranged at the bottom of the chamber. The size of the small opening varied from 0.01m to 0.05m. External radiation was achieved by electrically heating the walls and the ceiling of the combustion chamber. Two levels of external radiation were used during the experiments, namely 4.2kW/m^2 and 22.4kW/m^2.

In all 38 experiments were performed within the project. The conditions for each experiment are given in tables 6 to 11.

Table 6. Experimental conditions for tests with heptane.

HEPTANE					
Test Number	Substance	Amount burned (kg)	Diameter of fire (m)	Opening height (m)	External radiation (kW/m^2)
HEP001	Heptane	1	0.2	0.2	0
HEP002	Heptane	2	0.3	0.2	0

Table 7. Experimental conditions for tests with chlorobenzene.

CHLOROBENZENE					
Test Number	Substance	Amount burned (kg)	Diameter of fire (m)	Opening height (m)	External radiation (kW/m^2)
CB003	Chlorobenzene	-	0.2	0.2	0
CB004	Chlorobenzene	1.2	0.2	0.2	0
CB005	Chlorobenzene	1	0.3	0.2	0
CB006	Chlorobenzene	0.8	0.4	0.2	0
CB019	Chlorobenzene	2.1	0.2	0.2	0
CB020	Chlorobenzene	2.5	0.2	0.2	0
CB021	Chlorobenzene	2.3	0.2	0.2	4.2
CB022	Chlorobenzene	0.7	0.1	0.1+0.05*	4.2
CB023	Chlorobenzene	0.3	0.1	0.1+0.02*	4.2
CB024	Chlorobenzene	0.4	0.15	0.1+0.02*	4.2
CB025	Chlorobenzene	1.4	0.2	0.1+0.02*	4.2
CB026	Chlorobenzene	0.6	0.1	0.1+0.02*	22.4
CB027	Chlorobenzene	0.8	0.15	0.1+0.02*	22.4
CB028	Chlorobenzene	0.6	0.15	0.1+0.01*	22.4
CB029	Chlorobenzene	0.4	0.1	0.1+0.01*	22.4
CB030	Chlorobenzene	0.3	0.15	0.1+0.01*	22.4

** The opening was divided into two parts, 0.1m at the top and 0.05m, 0.02m and 0.01m respectively at the bottom.*

Table 8. Experimental conditions for experiments with TMTM.

TMTM					
Test Number	Substance	Amount burned (kg)	Diameter of fire (m)	Opening height (m)	External radiation (kW/m^2)
TMTM007	TMTM	1	0.2	0.2	0
TMTM008	TMTM	1	0.3	0.2	0
TMTM009	TMTM	1.5	0.4	0.2	0
TMTM010	TMTM	2.2	0.4	0.2	0
TMTM014	TMTM	2	0.4	0.2	0
TMTM037	TMTM	0.7	0.3	0.1+0.01*	22.4
TMTM038	TMTM	1.1	0.3	0.1+0.01*	22.4

** The opening was divided into two parts, 0.1m at the top and 0.01m at the bottom.*

Table 9. Experimental conditions for tests with CNBA.

CNBA					
Test Number	Substance	Amount burned (kg)	Diameter of fire (m)	Opening height (m)	External Radiation (kW/m^2)
CNBA016	CNBA	0.3	0.2	0.2	0
CNBA017	CNBA	2.3	0.3	0.2	0
CNBA018	CNBA*	1.6	0.3	0.2	0

** Polypropylene was added as ignition source.*

Table 10. Experimental conditions for tests with dimethoate.

DIMETHOATE					
Test Number	Substance	Amount burned (kg)	Diameter of fire (m)	Opening height (m)	External radiation (kW/m^2)
DIM011	Cyclohexanone + xylene	1	0.2	0.2	0
DIM012	Dimethoate	0.6	0.2	0.2	0
DIM013	Dimethoate	0.6	0.3	0.2	0
DIM015	Dimethoate	1.2	0.3	0.2	0

Table 11. Experimental conditions for tests with Nylon 6,6.

NYLON 6,6					
Test Number	Substance	Amount burned (kg)	Diameter of fire (m)	Opening height (m)	External radiation (kW/m^2)
NYL031	Nylon 6,6	0.3	0.1	0.1+0.01*	22.4
NYL032	Nylon 6,6	0.3	0.15	0.1+0.01*	22.4
NYL033	Nylon 6,6	0.5	0.2	0.1+0.01*	22.4
NYL034	Nylon 6,6	0.6	0.3	0.1+0.01*	22.4
NYL035	Nylon 6,6	1	0.4	0.1+0.01*	22.4
NYL036	Nylon 6,6	1.2	0.4	0.1	22.4

** The opening was divided into two parts, 0.1m at the top and 0.01m at the bottom.*

3 Calculations

A large amount of data was collected during each experiment. The data was recorded by means of a data logger. After the experiment the recorded data was processed and transformed to variables that could be interpreted and used as results from the performed tests. In the following sections, descriptions are given of the calculations performed during the evaluation of each experiment.

3.1 Mass loss and mass loss rate

The mass and the mass loss were measured with a load cell as described in section 2.2. The mass of the sample was registered every 5s and thus the mass loss was also calculated every 5s. This gives a very fluctuating curve. The turbulence in the room caused by the flow of air and combustion gases also influences the mass measurements. In order to make the influence of these fluctuations as small as possible the mass loss was calculated as the mean values over periods of various duration. In figure 7, examples are given from DIM013 with Dimethoate. Curve 1 is calculated with a mean value of the mass taken over 232s and curve 2 is calculated with a mean value over 72s. As can be seen the curve becomes much smoother when the period, over which the mean value is taken, is increased. As can be seen in figure 8, the mass loss is relatively constant, over a long period of the experiment. It is therefore possible to take the mean value over a long period, without making a large error in the calculation of the mass loss rate.

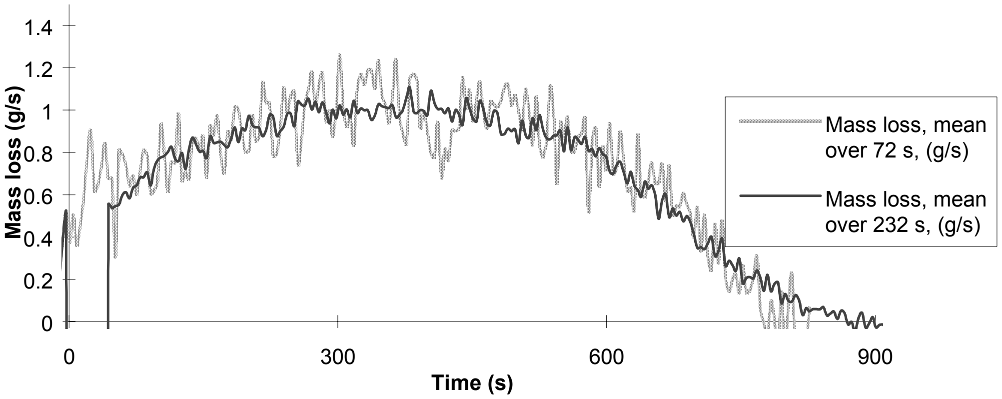


Figure 7. Mass loss as a function of time for DIM013 with Dimethoate.

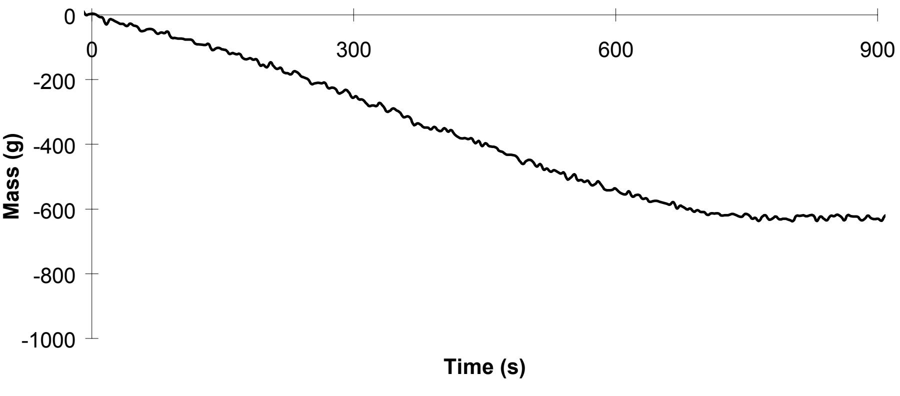


Figure 8. The mass of the sample, as a function of time for DIM013 with Dimethoate.

3.2 Equivalence ratio

The ventilation condition during the experiment has a great influence on the development of the fire. One way of describing the ventilation is to use the equivalence ratio or as it is often called the phi-value. The theoretical phi-value can be written as in equation [3.1]:

$$\phi = \left(\frac{\dot{m}_{fuel}}{\dot{m}_{O_2}} \right) / \left(\frac{\dot{m}_{fuel}}{\dot{m}_{O_2}} \right)_{stoich} \qquad [3.1]$$

Where the ratio between $\dot{m}_{fuel}$, the amount of fuel and $\dot{m}_{O_2}$, the amount of oxygen available, in the actual case is compared to the same ratio at stoichiometric conditions. $\dot{m}_{fuel}$ is determined by measuring the mass loss of the burned substance and massflow of oxygen entering the combustion chamber.

Experimentally the phi-value is measured with an apparatus called a phi meter. The principle of this equipment is described in section 2.3. The phi-value was determined from the phi meter reading by equation [3.2]:

$$\begin{aligned} &\phi = (X_{O_2} - X_m) / (X_0 \cdot (1 - X_m)) \\ &\phi = 1 \text{ stoichiometric combustion} \\ &\phi < 1 \text{ well - ventilated combustion} \\ &\phi > 1 \text{ under - ventilated combustion} \end{aligned} \qquad [3.2]$$

X_{O2} is the molar fraction of oxygen in the oxygen meter with extra oxygen, X_m is the scale value on the oxygen meter and X_0 is the concentration of oxygen in the surrounding air, normally 20.9 %. This measured phi-value can then be compared to the theoretical value.

The stoichiometric fuel/air mass ratio, commonly known as r, is given in kg_{fuel} per kg_{air}. r can be calculated from the reaction formula for complete combustion of the burned substance. The reaction formula for complete combustion of heptane is given below, [3.3]:

$$C_7H_{16}(l) + 11(O_2(g) + 3.76N_2(g)) \rightarrow 7CO_2(g) + 8H_2O(g) + 41.36N_2(g) \qquad [3.3]$$

This gives a value of r for heptane of $0.0662 kg_{fuel}/kg_{air}$. The value of r for the substances tested are given in Table 12.

Table 12. The stoichiometric fuel/air mass ratios for tested substances.

Substance	**r [kg_{fuel}/kg_{air}]**
Heptane, C_7H_{16}	0.0662
Chlorobenzene, C_6H_5Cl	0.1171
TMTM, $C_6H_{12}N_2S_3$	0.1264
Dimethoate, $C_5H_{12}NO_3PS_2$, formulation*	0.1145
Cyclohexanone, $C_6H_{10}O$ + xylene, C_8H_{11}**	0.0854
CNBA, $C_7H_4ClNO_4$	0.2551
Nylon 6,6, $C_{12}H_{22}N_2O_2$	0.0999

** Dimethoate was tested in a solution with 77% (by weight) cyclohexanone and 23% xylene*

*** The formulation consisted of 41% dimethoate, 45% cyclohexanone and 14% xylene.*

The r-values are calculated for complete combustion. This means that all carbon is transformed to carbon dioxide, CO_2 and all hydrogen is transformed to water, H_2O. Some of the tested substances contain other atoms as well. These are supposed to react as follows: Chlorine, Cl reacts to hydrogen chloride, HCl, nitrogen, N reacts to NO_2, phosphor, P reacts to H_3PO_4 and sulphur, S reacts to SO_2.

The phi-value can also be calculated from measurements of fuel mass loss, opening size and temperature of the air entering the combustion chamber and temperature of the combustion gases leaving the combustion chamber. The following equation, [3.4] from references [10, 11] has been used in comparisons between measured and calculated phi-values:

$$\phi = m_{fuel} \cdot 10^{-3} \cdot \left[h \cdot w \cdot \sqrt{h} \cdot \frac{2}{3} \cdot C_d \sqrt{2 \cdot g} \cdot \rho_0 \left(\left(1 - (T_0 / T_u)\right) / (1 + (T_u / T_0)^{1/3}\right)^3 \cdot r \right]^{-1/2} \qquad [3.4]$$

Phi-values have been calculated using the above expression for all experiments with a single opening. For the experiments with two small openings, this expression is not applicable. m_{fuel} is the mass loss of the fuel during the experiment given in [g/s]. C_d, the discharge coefficient is set to 0.68 in the calculations and ρ_0, the density of the surrounding air is taken as 1.2kg/m^3. An ambient temperature of 293K is used throughout the whole series of experiments and the temperature of the hot upper layer T_u is taken as a mean of the four upper thermocouples inside the combustion chamber. The factor 2/3 in the equation comes from the experience that the hot gases leaving the combustion chamber comes through the upper half to two thirds of the opening.

3.3 Combustion gas yields: CO_2, CO, NO_x and HC

The measured concentrations of CO_2, CO, NO_x and HC (unburned hydrocarbons) are presented as gas yields, Y_i [g/g]. The combustion gas yields were calculated using measurements of the total gas production, m_i [g] and the total mass of the sample burned, m_{fuel} [g], according to equation [3.5].

$$Y_i = \frac{m_i}{m_{fuel}} \qquad [3.5]$$

The carbon content of the fuel, Ψ_C [g/g] is known and thus the maximum yields, Ψ_i [g/g] of CO_2 and CO can be calculated. These values are given in Table 5. The maximum yields were calculated according to equations [3.6] and [3.7] using the molecular weights, M_{CO2} = 44.01g/mole, M_{CO} = 28.01g/mole and M_C = 12.01g/mole respectively. The assumption is made that all carbon is converted to CO_2 and CO.

$$\Psi_{CO_2} = \Psi_C \cdot \frac{M_{CO_2}}{M_C} \qquad [3.6]$$

$$\Psi_{CO} = \Psi_C \cdot \frac{M_{CO}}{M_C} \qquad [3.7]$$

The theoretical yields of NO_2 for TMTM, dimethoate, CNBA and nylon are calculated accordingly assuming all nitrogen in the fuel to be converted to NO_2. The calculation for nylon is given below as an example, equation [3.8].

$$\Psi_{NO_2} = 2 \cdot \frac{M_{NO_2}}{M_{nylon}} \qquad [3.8]$$

M_{NO2}= 46.01g/mole and M_{nylon}= 226.4g/mole.

The theoretical yields of HCl for chlorobenzene and CNBA and of SO_2 for TMTM and dimethoate are calculated following the same procedure.

The gas analysis equipment measures unburned hydrocarbons with a boiling point below 200°C. The hydrocarbons are calculated as propane equivalents. Hydrocarbons with a boiling point over 200°C, soot particles etc., are defined as the survival fraction and are not included in the unburned hydrocarbons. The amount of soot produced is also calculated. This procedure is described in section 3.5.

3.4 Rate of heat release and total heat release

The heat released during the experiments was calculated using the standard, oxygen consumption, calorimetry method [7, 10]. Concentrations of O_2, CO_2 and CO were used for the calculations.

The volume flow $\dot{V}$ [m^3/s], at STP, in the duct, equation [3.9] was calculated using the exhaust duct area A [m^2], the pressure difference in the exhaust duct Δp [Pa] and the gas temperature in the duct T_e [K]. The ratio between the average mass flow per unit area and the mass flow per unit area in the centre of the exhaust duct is 0.9. The calibration constant for the bi-directional Pitot tube is 1.08.

$$\dot{V} = \frac{22.4 \cdot A \cdot 0.9}{1.08 \cdot \sqrt{\frac{\Delta p}{T_e}}} \qquad [3.9]$$

The rate of heat release q [kW] was calculated using the following expression, equation [3.10]:

$$q = \Delta H_{C,ox} \cdot 1.31 \cdot 1000 \cdot \frac{\Phi}{1 + \Phi(\alpha - 1)} \dot{V} \cdot X^0_{O_2} \qquad [3.10]$$

Where $\Delta H_{C,ox}$ [kJ/gO_2] is the heat released per unit mass oxygen consumed. The values of the various constants can be found in Table 5. The density of oxygen is 1.31kg/m^3. The expansion factor α is set to 1.1. Φ is the oxygen depletion factor, i.e. the fraction of the incoming air that is fully depleted of its oxygen. Φ can be calculated using the expression in equation [3.11]:

$$\Phi = \frac{X^0_{O_2}(1 - X_{CO_2}) - X_{O_2}(1 - X^0_{CO_2})}{X^0_{O_2}(1 - X_{O_2} - X_{CO_2})} \qquad [3.11]$$

Where X_i^0 is the mole fraction of gas i in the incoming air and X_i the mole fraction of gas i in the exhaust duct. $X^0_{O_2}$ was set to 0.209.

The total heat release is taken, as the integrated value of the rate of heat release, during the entire experiment. This gives the energy in [kJ].

3.5 Smoke production

The smoke production can be presented in a number of ways. In this report, the extinction coefficient K [1/m] is defined as in [3.12] from reference [12]:

$$K = \sigma_m \cdot m \qquad [3.12]$$

Where σ_m is the extinction area per unit mass [m^2/g] and m is the mass concentration of the smoke aerosol [g/m^3]. From the measurements in the duct, K is calculated as given by equation [3.13] below:

$$K = \left(\frac{1}{L}\right) \cdot ln\left(\frac{I_0}{I}\right) \qquad [3.13]$$

Where L [m] is the beam length of the light through smoke. I_0 [-] is the light intensity without smoke and I [-] is the light intensity during the test. σ_m is also determined from the measurements in the duct and from the samples of soot collected during the experiments, as given in equation [3.14].

$$\sigma_m = K \cdot (V \cdot (273 + T_e) / 273) / m_{soot} \qquad [3.14]$$

Where V is the volume of gas [m^3] that has flown through the filter, T_{duct} is the temperature in the duct and m_{soot} is the amount of soot in [g] which has been collected on the filter during the experiment. σ_m is determined for the tested substances and the values are given in table21.

The smoke production is also given as a yield in [g/g]. This means gram soot produced per gram substance burned.

The smoke production given as [g/s] can be calculated in the following way, equation [3.15]:

$$K \cdot \dot{V} \cdot ((T_e + 273) / 273) \cdot (1 / \sigma_m) \qquad [3.15]$$

The smoke production in [g/s] is divided by the substance mass loss also given in [g/s]. This gives the smoke yield in g soot produced per gram substance burned.

4 Results

The work within WP3 of the TOXFIRE project comprises 38 medium scale experiments with 6 different substances, 3 levels of external radiation, 5 fire diameters and 3 different opening heights. In this section, the results will be given in tables and for selected experiments as diagrams. A comprehensive report of the results, from all experiments in the form of diagrams is given as an appendix to the report.

One important variable for characterising the results from combustion experiments in enclosures is the degree of ventilation here given as the equivalence ratio or the phi-value. The phi-value varies between the experiments and during the course of a single experiment. This has been dealt with in the following way: During each experiment, periods with relatively constant phi-value have been chosen and the other measured variables have been evaluated during these periods.

4.1 Phi-values

As mentioned earlier the phi-value gives a measure of the degree of ventilation, during the course of the fire. One objective with the experiments was to study how a variation in ventilation influences the burning conditions and hence the production of combustion gases. The phi-value varies between the experiments, and during the course of a single experiment since it is difficult to achieve long periods with steady state burning, in the type of experimental set up that has been used in the reported experiments. The measured phi-value varied, between 0.04 and 1.4 in the conducted experiments. A phi-value over 1.0 indicates poorly ventilated conditions. During the performance of the experimental series, it was found that the conditions and the design of the experimental apparatus made it difficult to reach high phi-values, at least for the low-energy content substances tested. Efforts were made to force the fire into low ventilation conditions by increasing the exposed area of the substance burned. The result of this was a pulsating fire and no stable conditions.

Comparisons were made between the measured and the theoretical phi-values when this was feasible. For experiments where the opening was divided into one upper and one lower part the theoretical phi-value has not been calculated. The methods of calculation for measured and theoretical phi-values are given in section 3.2. In figures, 9 and 10 examples are given of comparisons between measured and theoretical phi-values. Results for all experiments are given in tables 13 to 18.

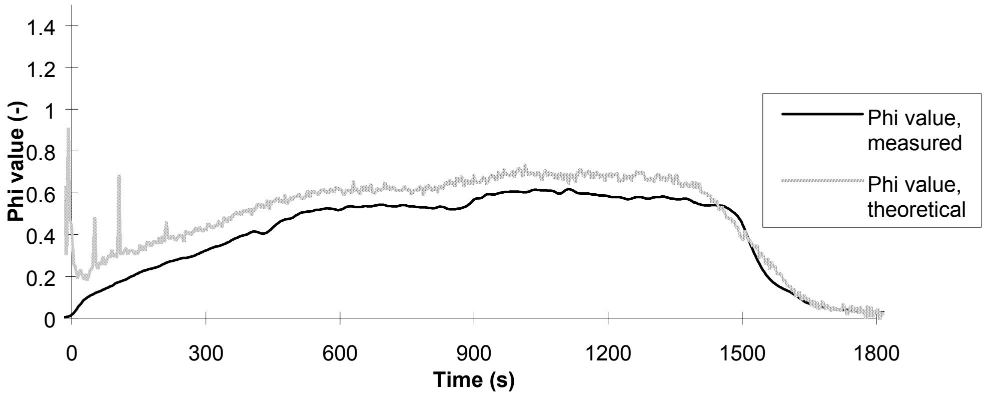


Figure 9. Comparisons between measured and theoretical phi-value for experiment CB019 with chlorobenzene.

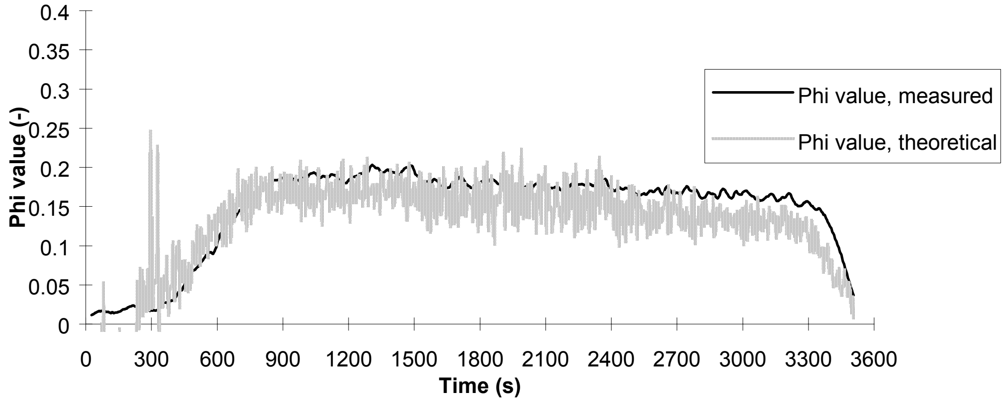


Figure 10. Comparisons between measured and theoretical phi-value for experiment TMTM007 with TMTM.

4.2 Temperatures inside the combustion chamber

The temperature was measured on a great number of locations inside the combustion chamber as described in section 2.2. Surface temperatures on the walls and in the ceiling as well as gas temperatures were measured. The mean upper temperature for the periods with constant phi-value is given in tables 13 to 18 and in the appendix. In figures 11 and 12 examples are given of surface temperatures and gas temperatures for an experiment with nylon6, 6.

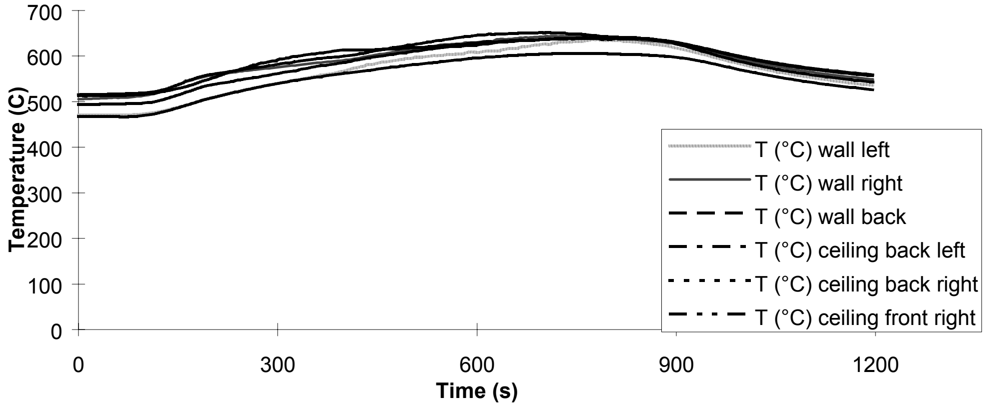


Figure 11. Surface temperature inside the combustion chamber for NYL035 with nylon6,6.

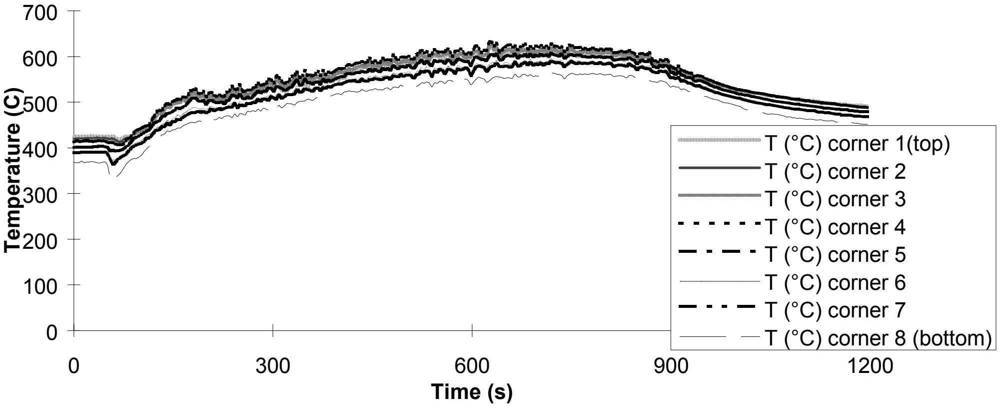


Figure 12. Gas temperature inside the combustion chamber for NYL035 with nylon6, 6.

4.3 Rate of heat release and total heat release.

The amount of heat produced was measured during all experiments. The oxygen consumption technique was used to monitor the heat output. The rate of heat release for all experiments is given in tables 13 to 18 and in the appendix. An example of a heat release curve is also given in figure 13 for an experiment with TMTM. In figure 14 the total energy released during experiment TMTM010 is given as a function of time.

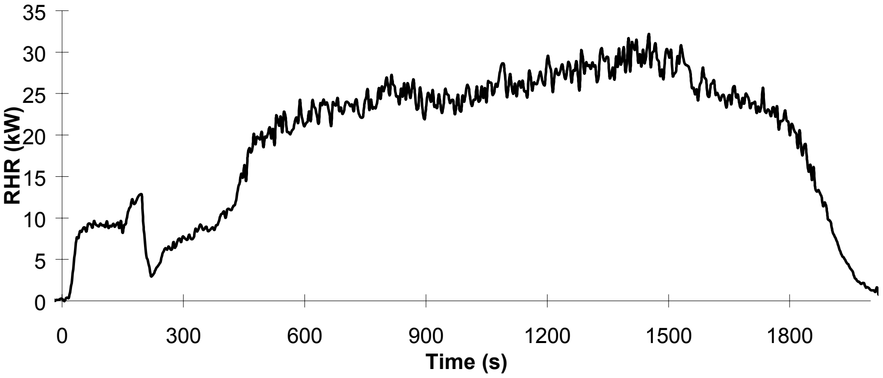


Figure 13. The RHR for experiment TMTM010 with TMTM.

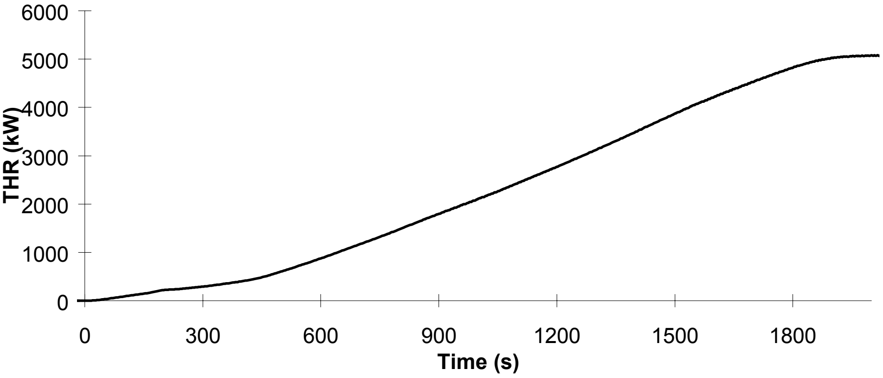


Figure 14. Total energy released during experiment TMTM010 with TMTM.

4.4 Yields of CO_2, CO, HC, NO_x and smoke

During the experiments the concentrations of CO_2, CO, HC, NO_x and smoke were measured continuously in the exhaust duct. From these levels of concentration the yields of the species could be determined by dividing the produced amounts with the mass burning rate thus giving the yield in grams of the species produced per gram burned substance. The yields are given in tables 13 to 18 and in the appendix, the yields are presented as a function of time. The yields of CO_2 and CO were determined in all experiments. The yield of HC was difficult to measure in the experiments with TMTM since hardly any soot or unburned hydrocarbons could be detected during the experiments. NO_x was mainly detected in the experiments with nitrogen containing substances such as CNBA, TMTM, dimethoate and nylon 6,6. For the other substances the amounts of NO_x were very low.

4.5 Recovery of carbon

The amount of carbon showing up among the totality of the combustion products should be equal to the amount of carbon leaving the fuel. The carbon in the products can show up as CO_2, CO, unburned hydrocarbons or as soot. In figure 15 an example of carbon recovery from experiment CB023 with chlorobenzene is presented. As can be seen, the main part of carbon is found in the smoke and as unburned hydrocarbons.

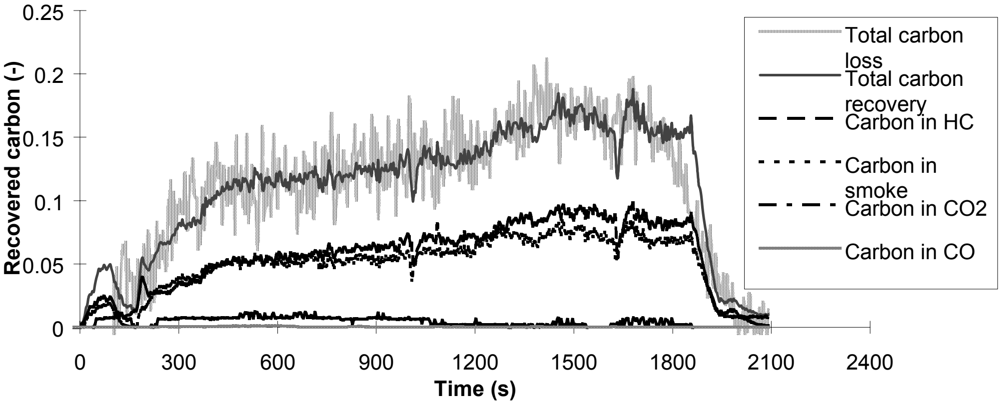


Figure 15. Recovered carbon for experiment CB023 with chlorobenzene.

Table 13. Results from experiments with heptane.

HEPTANE										
Test number	Phi-value, measured	Phi-value, theoretical	Upper layer temp (°C)	Mass loss (g/s)	RHR (kW)	Yield CO_2* (g/g)	Yield CO** (g/g)	Yield NOx (g/g)	Yield HC (g/g)	Yield soot (g/g)
HEP001	0.8	0.8	474	1.1	28.0	2.09 68%	0.007 0.4%	0.0004	0.002	0.012
HEP002	1.4	1.6	562	2.2	34.6	1.24 40%	0.168 8%	0.0001	0.22	0.007

* The yield of CO_2 is given in g CO_2 produced/g substance burned and in % of the amount theoretically possible.
** The yield of CO is given in g CO produced/g substance burned and in % of the amount theoretically possible.

Table 14. Results from experiments with chlorobenzene.

CHLOROBENZENE										
Test number	Phi-value, measured	Phi-value, theoretical	Upper layer temp (°C)	Mass loss (g/s)	RHR (kW)	Yield CO_2* (g/g)	Yield CO** (g/g)	Yield NOx (g/g)	Yield HC (g/g)	Yield soot (g/g)
CB004	0.23	0.28	138	0.5	6.3	0.08 2%	0.044 2.9%	0.0002	0.208	0.163
CB005	0.28	0.43	180	0.9	7.8	0.36 10%	0.051 3.4%	0.0001	0.195	0.102
"	0.54	0.56	274	1.4	13.8	0.74 20%	0.063 4.2%	0.0002	0.169	0.072
"	0.74	0.80	343	1.9	17.8	0.82 22%	0.059 4.0%	0.0002	0.130	0.041
CB019	0.53	0.61	309	1.5	7.5	0.89 24%	0.061 4.1%	-	0.160	0.061
"	0.60	0.69	350	1.7	10.6	0.98 27%	0.063 4.2%	-	0.131	0.046
"	0.57	0.66	370	1.6	8.6	0.89 24%	0.060 4.0%	-	0.136	0.059
CB020	0.58	0.63	302	1.5	24.0	1.61 44%	0.122 8.2%	-	0.442	0.087
"	0.65	0.72	344	1.7	26.3	1.50 41%	0.114 7.7%	-	0.315	0.072
"	0.72	0.77	403	1.9	29.1	1.50 41%	0.134 9.0%	-	0.452	0.095
CB021	0.65	0.69	381	1.7	24.2	1.66 45%	0.118 7.9%	-	0.123	0.088
"	0.92	0.73	448	1.8	34.3	2.07 57%	0.173 12%	-	0.120	0.079
CB023	0.39	-	215	0.2	0.7	0.16 4%	0.002 0.1%	-	0.402	0.292
"	0.40	-	230	0.2	0.6	0.04 1%	0.000 -	-	0.407	0.305
CB024	0.16	-	242	0.4	0.4	-	-	-	-	0.263
"	0.19	-	255	0.5	0.8	-	-	-	-	0.201
"	0.23	-	273	0.6	0.9	-	-	-	-	0.223
CB025	0.50	-	345	1.3	12.9	1.07 29%	0.079 5.3%	-	0.266	0.163
"	0.83	-	405	1.9	26.6	1.44 39%	0.146 9.8%	-	0.383	0.111
CB026	0.27	-	466	0.9	12.1	1.50 41%	0.100 6.7%	-	0.186	0.166
"	0.71	-	505	1.5	38.3	2.38 65%	0.283 19%	-	0.264	0.128
CB027	0.48	-	493	1.6	19.6	1.22 33%	0.223 15%	-	0.023	0.121
”	0.90	-	530	2.1	37.0	1.64 45%	0.457 31%	-	0.027	0.071
”	0.86	-	544	2.0	34.5	1.62 44%	0.456 31%	-	0.021	0.072

* The yield of CO_2 is given in g CO_2 produced/g substance burned and in % of the amount theoretically possible.

** The yield of CO is given in g CO produced/g substance burned and in % of the amount theoretically possible.

Table14 continued. Results from experiments with chlorobenzene.

CHLOROBENZENE										
Test number	Phi-value, measured	Phi-value, theoretical	Upper layer temp (°C)	Mass loss (g/s)	RHR (kW)	Yield CO$_2$* (g/g)	Yield CO** (g/g)	Yield NOx (g/g)	Yield HC (g/g)	Yield soot (g/g)
CB028	0.41	-	476	-	17.0	1.08 30%	0.089 6.0%	0.0001	0.104	0.046
”	0.98	-	510	7.8	24.2	0.30 8.0%	0.035 2.3%	0.0000	0.121	0.023
CB029	0.32	-	480	1.1	18.8	1.66 45%	0.112 7.5%	0.0006	0.314	0.083
”	0.27	-	488	1.1	18.6	1.55 42%	0.098 6.6%	0.0006	0.196	0.075
”	0.15	-	492	0.8	16.1	1.88 51%	0.11 7.3%	0.0007	0.253	0.116
CB030	0.30	-	486	1.1	12.4	1.31 36%	0.064 4.3%	0.0002	0.388	0.098
”	0.40	-	495	1.1	18.2	1.73 47%	0.11 7.4%	0.0003	0.495	0.096

* The yield of CO$_2$ is given in g CO$_2$ produced/g substance burned and in % of the amount theoretically possible.

** The yield of CO is given in g CO produced/g substance burned and in % of the amount theoretically possible.

Table 15. Results from experiments with TMTM.

TMTM										
Test number	Phi-value, measured	Phi-value, theoretical	Upper layer temp (°C)	Mass loss (g/s)	RHR (kW)	Yield CO$_2$* (g/g)	Yield CO** (g/g)	Yield NOx*** (g/g)	Yield HC (g/g)	Yield soot (g/g)
TMTM007	0.18	0.15	180	0.4	5.8	-	0.001 0.12%	0.0363 8.2%	-	-
TMTM008	0.40	0.35	289	0.9	15.6	0.52 41%	0.001 0.12%	0.0240 5.4%	-	-
TMTM009	0.62	0.54	386	1.4	26.8	0.75 59%	-	0.0106 2.4%	-	-
TMTM010	0.71	0.60	446	1.6	28.0	0.91 71%	-	0.0099 2.2%	-	-
TMTM014	0.62	0.53	334	1.4	18.3	0.78 61%	-	0.0106 2.4%	-	-
"	0.70	0.57	426	1.5	21.1	0.89 70%	0.000 -	0.0118 2.7%	-	-
TMTM037	0.77	-	609	1.8	41.9	1.11 87%	0.095 12%	0.0181 4.1%	0.074	-
"	0.86	-	618	1.8	45.3	1.18 92%	0.132 16%	0.0264 6.0%	0.121	-
TMTM038	0.90	-	602	2.1	46.7	0.90 70%	0.176 21%	0.0295 6.7%	0.192	-

* The yield of CO$_2$ is given in g CO$_2$ produced/g substance burned and in % of the amount theoretically possible.

** The yield of CO is given in g CO produced/g substance burned and in % of the amount theoretically possible.

*** The yield of NO$_x$ is given in g NO$_x$/g substance burned and in % of the amount theoretically possible.

Table 16. Results from experiments with CNBA

CNBA										
Test number	Phi-value, measured	Phi-value, theoretical	Upper layer temp (°C)	Mass loss (g/s)	RHR (kW)	Yield CO$_2$* (g/g)	Yield CO** (g/g)	Yield NOx*** (g/g)	Yield HC (g/g)	Yield soot (g/g)
CNBA016	0.04	0.06	78	0.3	-	0.30 19%	0.689 70%	0.0856 38%	0.006	0.127
”	0.16	0.06	187	0.4	13.4	2.76 1.8%	0.755 77%	0.0547 24%	0.047	0.131
CNBA017	0.13	0.16	177	1.2	0.9	0.47 31%	0.071 7.2%	0.0971 43%	0.024	0.150
”	0.24	0.25	310	2.0	24.3	2.21 >100%	0.114 12%	0.0551 24%	0.044	0.165
”	0.16	0.18	209	1.3	1.7	0.47 31%	0.062 6.3%	0.0881 39%	0.026	0.140
CNBA018	0.17	-	214	0.1	17.0	-	-	-	0.075	0.041
”	0.23	0.17	216	1.3	7.0	0.528 34%	0.039 4%	0.0003 0.13%	0.036	0.121
”	0.24	0.10	301	0.8	24.0	2.046 >100%	0.050 5%	0.0237 10%	0.026	0.103

* The yield of CO$_2$ is given in g CO$_2$ produced/g substance burned and in % of the amount theoretically possible.

** The yield of CO is given in g CO produced/g substance burned and in % of the amount theoretically possible.

*** The yield of NO$_x$ is given in g NO$_x$/g substance burned and in % of the amount theoretically possible.

Table 17. Results from experiments with dimethoate.

DIMETHOATE										
Test number	Phi-value, measured	Phi-value, theoretical	Upper layer temp (°C)	Mass loss (g/s)	RHR (kW)	Yield CO$_2$* (g/g)	Yield CO** (g/g)	Yield NOx*** (g/g)	Yield HC (g/g)	Yield soot (g/g)
DIM011	0.22	-	192	0.4	6.8	0.48 13%	0.002 0.19%	0.0008 0.27%	0.012	0.070
”	0.44	-	333	0.8	13.6	1.19 33%	0.014 1.4%	0.0007 0.23%	0.013	0.057
DIM012	0.06	0.16	191	0.3	7.6	0.18 4.9%	0.027 2.6%	0.0010 0.33%	0.014	0.081
”	0.20	0.19	287	0.6	11.5	0.96 26%	0.010 0.97%	0.0014 0.47%	0.010	0.064
DIM013	0.55	0.42	351	1.0	14.3	1.20 33%	0.022 2.1%	0.0012 0.40%	-	0.046
DIM015	0.48	0.37	309	0.8	12.9	1.68 46%	0.022 2.1%	0.0006 0.20%	0.018	0.055
”	0.73	0.55	429	1.3	21.5	1.7 46%	0.023 2.2%	0.0006 0.20%	0.006	0.013
”	0.94	0.61	490	1.5	27.1	1.93 53%	0.031 3.0%	0.0010 0.33%	0.008	0.002

* The yield of CO$_2$ is given in g CO$_2$ produced/g substance burned and in % of the amount theoretically possible.

** The yield of CO is given in g CO produced/g substance burned and in % of the amount theoretically possible.

*** The yield of NO$_x$ is given in g NO$_x$/g substance burned and in % of the amount theoretically possible.

Table 18. Results from experiments with Nylon 6,6

NYLON 6,6										
Test number	Phi-value, measured	Phi-value, theoretical	Upper layer temp (°C)	Mass loss (g/s)	RHR (kW)	Yield CO_2* (g/g)	Yield CO** (g/g)	Yield NOx*** (g/g)	Yield HC (g/g)	Yield soot (g/g)
NYL031	0.09	-	460	0.2	5.2	3.387 >100%	0.004 0.27%	0.2904 71%	0.004	0.043
”	0.05	-	454	0.1	1.6	1.309 56%	0.001 0.07%	0.3046 75%	0.009	0.114
NYL032	0.04	-	459	0.1	0.2	-	-	0.2137 53%	0.007	0.025
”	0.04	-	465	0.1	4.4	2.856 >100%	0.002 0.13%	0.2309 57%	0.010	0.049
NYL033	0.70	-	519	0.9	28.9	2.955 >100%	0.159 11%	0.0289 7.1%	0.075	0.022
NYL034	0.16	-	498	0.5	13.6	2.306 98%	0.077 5.2%	-	0.012	0.082
”	0.16	-	507	0.5	14.1	2.488 >100%	0.069 4.6%	-	0.017	0.091
NYL035	0.91	-	587	1.4	38.3	2.349 100%	0.120 8.1%	0.0166 4.1%	0.135	0.021
”	0.77	-	603	1.5	42.8	2.493 >100%	0.151 10%	0.0214 5.3%	0.280	0.012
”	0.86	-	613	1.4	37.3	2.375 >100%	0.125 8.4%	0.0190 4.7%	0.214	0.018

* The yield of CO_2 is given in g CO_2 produced/g substance burned and in % of the amount theoretically possible.
** The yield of CO is given in g CO produced/g substance burned and in % of the amount theoretically possible.
*** The yield of NO_x is given in g NO_x/g substance burned and in % of the amount theoretically possible.

4.6 Gas analysis

As reported above a number of common combustion gases have been detected on line. A large number of other substances are also produced during the combustion process. One important task in this project has been to try to identify these substances and to be able to compare the substances produced in one scale with substances produced in the other studied scales. The comparisons with other scales will be reported elsewhere. Only the results from the studies in medium scale are reported here. In table 23 most of the substances that where found in the GC-MS analysis are reported and in table 19 the ten most frequently appearing substances are given. It was possible to make quantitative analysis of a few of the gas samples. The results of the quantitative GC-MS analysis are given in table 20. In figure 16 an example of a spectrum from GC-MS is given. As can be seen the main component is tetra methyl thiourea, this is a compound very similar to TMTM.

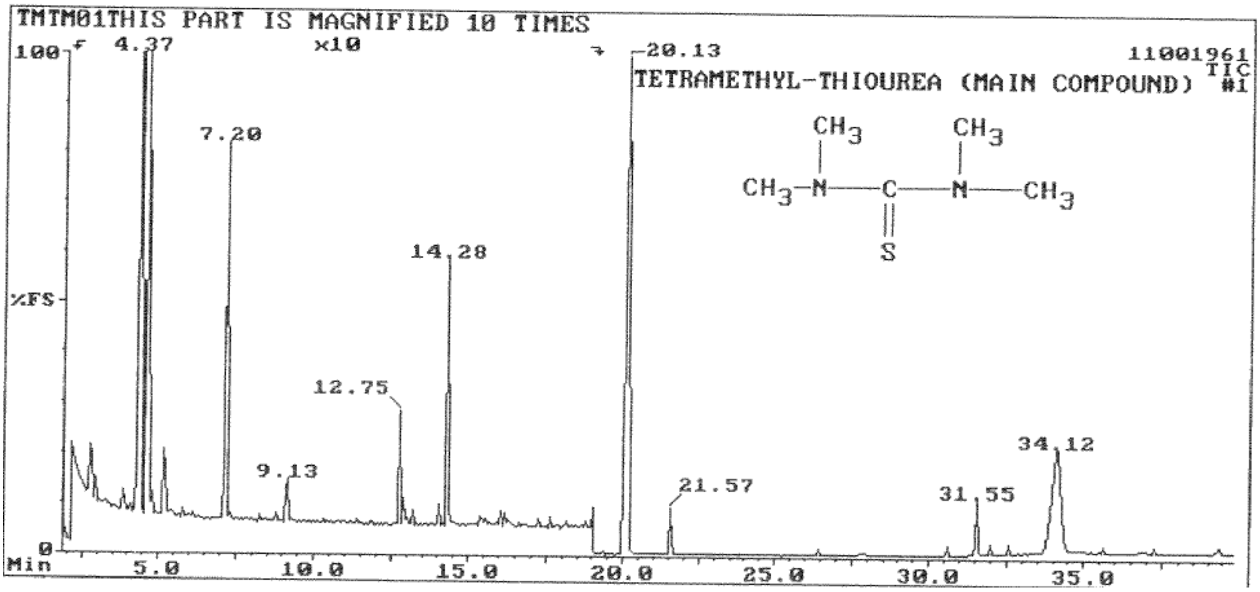


Figure 16. Spectrum from GC-MS analysis of sample from an experiment with TMTM.

Table 19. Compounds, most frequently detected in GC-MS analysis of gas samples

Detected compound	**Compound found in number of samples/samples analysed**	**Compound detected in samples from experiments with**
Naphthalene, $C_{10}H_8$	17 of 21	Chlorobenzene, TMTM, dimethoate, CNBA, Nylon
Benzene, C_6H_6	16 of 21	Chlorobenzene, TMTM, dimethoate, CNBA, Nylon
Toluene, C_7H_8	14 of 21	Chlorobenzene, TMTM, dimethoate, CNBA, Nylon
Heptadecane, $C_{17}H_{36}$	10 of 21	Chlorobenzene, TMTM, CNBA, Nylon
Tetramethyl-thiourea, $C_5H_{12}N_2S$	10 of 21	TMTM, dimethoate
Thiram, $C_6H_{12}N_2S_4$	8 of 21	TMTM
Chlorobenzene, C_6H_5Cl	7 of 21	Chlorobenzene, CNBA
Phenol, C_6H_6O	7 of 21	Chlorobenzene, TMTM, CNBA
Cyclooctatetraene, C_8H_8	7 of 21	TMTM, dimethoate
Methanethioamide, CH_3NS	7 of 21	TMTM

Table 20. Amounts of compounds detected in GC-MS analysis of gas samples

	Sample description, Yield of detected compound [mg/g burned]										
Detected compound	**CB 005**	**CB 019**	**CB 023**	**TMTM 014**	**TMTM 038**	**DIM 011**	**DIM 013**	**CNB A017**	**CNBA 018**	**NYL 032**	**NYL 034**
Benzene	0.8	0.7	1							8.4	12
Toluene		0.6				20	17			34	40
Chlorobenzene	30	10	31					11	14		
Chlorophenol									9		
2-chloro-benzonitrile								2	8		
Naphthalene	0.9		4					8	13	17	2
2,6,11-trimethyl-dodecane										0.6	
2-methyl-1-(1,1-dimethyl)propanoic acid	0.7										
Eicosane	0.7		2								
Benzonitrile									3		
Methyl-ester thiocyanic acid				4	2						
Tetramethyl-thiourea				75	71						
Thiram				0.9	1.1						
Xylene						50	76				
Cyclohexanone						32	39				

Samples of soot were also collected during the experiments, these soot samples were weighed, and from these measurements, the smoke extinction areas have been determined according to the procedure described in section 3.5. The values of the smoke extinction area for the tested substances are given in table 21. The values presented in table 21 are mean values for all experiments performed with each substance.

Table 21. Smoke extinction area for tested substances.

Substance	**Smoke extinction area (m^2/g)**
Chlorobenzene	9.5
TMTM	0.7*
Dimethoate	12.6
CNBA	8.3
Nylon-6,6	9.5

** This value is not to be taken as the smoke extinction coefficient for TMTM it only indicates that very small amounts of smoke are formed in the experiments with TMTM.*

The solutions in the impinger bottles were analysed with ion chromatography and for the tests with chlorobenzene and with CNBA, they were analysed with respect to content of HCl. When comparing the amount of HCl formed during combustion with the maximum amount of HCl that can be produced from chlorobenzene, given in table 22, it is found that the majority of Cl in chlorobenzene goes into formation of HCl. In addition, for CNBA a large portion of the Cl is transformed to HCl during the combustion. For both chlorobenzene and CNBA the main part of the remaining Cl is to be found in chlorobenzene that either survives the combustion or is formed during combustion. In table 23, the compounds that were found in the GC-MS analysis are presented. For chlorobenzene and CNBA, it can be seen that other complex chlorine containing compounds are formed as well but these account for minor parts of the total Cl content.

Table 22. Detected amount of HCl in combustion gases from experiments with CNBA and chlorobenzene

Test number	**Detected amount HCl Mg HCl/g burned substance**	**Theoretical amount HCl mg HCl/g burned substance**
CNBA018	120.4	180.9
CB022	279.1	325.2
CB023	293.8	325.2
CB025	378.0	325.2

Table 23. Compounds found with GC-MC analysis, in the combustion gases.

Compound	**Chlorobenzene**					**TMTM**								**Dimethoate**				**CNBA**		**Nylon**	
Sample description	005	019	022	023	025	007	008	009	010	014	036	037	038	011	012	013	015	017	018	032	034
benzene	x	x	x	x	x			x			x	x	x	x	x	x	x	x	x		x
toluene	x			x		x	x		x	x	x	x	x	x		x			x	x	x
tetracloroethene	x			x																	
clorobenzene	x	x	x	x	x													x	x		
ethynylbenzene	x															x	x		x		
etenylbenzene	x			x																	
phenol	x		x	x						x	x		x						x		
clorophenol	x			x														x	x		
1,3-diclorobenzene	x																	x	x		
1,4-diclorobenzene	x																	x	x		
1H-purine 2,6-	x																				
1,2-dichlorobenzene	x			x																	
1-chloro-4-etynyl-benzene	x			x																	
1-chloro-3-etynyl-benzene	x																		x		
2-cloro-benzonitrile																		x	x		
naphtalene	x		x	x		x	x	x	x		x	x	x	x	x	x	x	x	x		x
1,2,4-trichlorobenzene	x																				
dodecane										x											x
4-chlorophenol	x		x																x		
1-methyl naphtalene	x					x		x													
1-methyl naphtalene	x		x	x																	
1-ethylidene 1-H indene	x																				
2,4,6-trimethyloctane	x		x			x				x	x		x								
1-chloronaphtalene	x		x																		
2-chloronaphtalene																		x	x		
1-ethylnaphtalene	x																				
biphenylene	x		x	x												x					
3-phenyl-2-propenylchloride	x																				
1,8-dimethylnaphtalene	x																				
acenaphthylene	x			x																	
3-methyl-tridecane	x			x																	
2,6,11-trimethyl-dodecane																				x	
2-meth.-,1-(1,1-dimeth.eth.)propanoic acid	x																				
dimethyl-heptadecane																			x		
allyl ethyl ester phthalic acid	x																				
3,6-dimethylundecane	x																				
2,5,6-trimethyldecane	x																				
heptadecane	x		x	x				x	x	x	x		x						x	x	
octanoic acid	x																				
eicosane	x			x						x									x		
3-(ethenyloxy)methyl-heptane	x			x																	
1-hexadecanol	x		x	x																	
buth.oct.ester1,2-benzendicarb.acid	x		x																		
dimethylphenyl ester benzoic acid	x																			x	
buthyl 2-methylpropyl ester -	x																				
1,2 benzene dicarboxylic acid	x		x							x											
diisooct.ester 1,2 benzenedicarb.acid	x		x	x																	
1,3,5,7-cyclooctatetraene						x	x	x			x		x		x	x					
benzonitrile								x	x		x							x	x		x

Table 23. (continued)

Compound	**Chlorobenzene**					**TMTM**								**Dimethoate**				**CNBA**		**Nylon**	
Sample description	005	019	022	023	025	007	008	009	010	014	036	037	038	011	012	013	015	017	018	032	034
2,6-(1,1-isobut.)-4-methylcarbamatphenol											x										
1,2-propendienylbenzen											x										
bis(2-ethylhexyl)phtalat											x									x	
2-methyldodecane							x	x	x		x		x								
2-methyl-nonadecane																					x
6-ethyl-2-methyl-octane																					x
2,8-dimethyl-undecane										x											x
2-meth-,1-(1,1-dimeth.eth)-2-meth-1,3-prop.aci		x	x	x	x																
diethyl phtalat		x	x	x	x																
dioctyl ester		x		x	x																
6-methyl-octadecane															x		x				
hexane										x											
methyl ester thiocyanic acid										x											
nonanal						x				x	x	x	x								
ethyl-benzaldehyde										x											
tetramethyl-thiourea						x	x	x	x	x	x	x	x	x		x					
tetradecane										x											
thiram						x	x	x	x	x	x	x	x								
trimethyl-thiourea						x				x		x									
4-(2,2,3,3-tetramethylbutyl)-phenol										x											
nonyl-phenol										x											
docosane										x											
dibenzofuran																		x	x		
xylene														x	x	x	x	x	x		
cyclohexanone														x	x	x	x				
1-ethyl-3-methyl-benzene																x					
benzaldehyde																x					
1H-indene														x		x					
1-methyl-1H-indene																x					
1-ethylidiene-1H-indene																x					
thiophene						x	x	x					x								
methyl ester, thiocyanic acid								x	x		x	x									
(dimethylamino)-acetonitrile								x													
dimethyl-cyanamide								x													
N,N-dimethyl-methanethioamide						x	x	x	x		x	x	x								
N,N-dimethyl-benzenamide								x													
benzothiophene							x	x		x			x								

5 Discussion

The results indicate that the equivalence ratio or as it is often referred to the phi-value is a useful variable when it comes to means of characterising enclosure fires. In the series of experiments presented here, it has been shown that the experimentally measured and the calculated phi-values are in good agreement. The phi-values vary between 0.04 to 1.4 in the experiments. Attempts were made to reach higher phi-values. These attempts were however not successful. This was found to depend mainly on the design of the experimental set up. When the fire was forced into lower ventilation conditions the fire quickly reached unstable and uncontrollable conditions. One typical result was a pulsating fire with long flames coming out of the opening.

The measurements of the phi-values were made with equipment suggested by Babrauskas et al [7]. In order to make good measurements in a repeatable way some parts of the equipment had to be redesigned. The reactor was originally made of quarts glass but this material was too brittle to withstand a long series of experiments and was replaced by a stainless steel reactor. The suggested catalyst had a working temperature of about 1000°C, which is a very high temperature to have in an environment where pure oxygen and combustible gases of various compositions are mixed. The original catalyst was exchanged for a catalyst working at around 400°C.

The rate of heat release was measured in all experiments using the oxygen consumption technique. Measured RHR ranged from 0.4kW to 47kW, depending on the substance burned and whether external radiation was imposed or not.

The yields of CO_2, CO, NO_x, HC and soot were determined in all experiments where possible. For CO_2, CO and NO_x a comparison was also made between the measured yield and the highest yield theoretically possible. For heptane the yield of CO_2 was over 40% and the yield of CO under 10% of the theoretical maximum yields. The yield of NO_x was very low as can be expected for a non-nitrogen compound. The yields of HC and soot were low and this is in agreement with the general observations during the experiments.

Results are presented from 13 experiments with chlorobenzene. For chlorobenzene, the CO_2 yield covers a wide range, from 1% to 65% of the theoretically possible. The yield of CO goes up to 31% of the maximum theoretical value. It has not been possible to establish any relationships between the produced amounts of CO_2 and the phi-values or the RHR during the experiments. The yield of unburned hydrocarbons was less than 0.5g/g substance burned during all tests with chlorobenzene.

Thirteen experiments were performed with TMTM. The CO_2 production varied between 41% and 92% of the theoretical values in all experiments. The production of CO was extremely low. In fact, no CO was detected except for the experiments with external radiation where 12% to 21% of the theoretically possible amount of CO was detected. TMTM is a nitrogen containing substance and hence a production of NO_x could be anticipated during the combustion. NO_x was also detected during the experiments but the yield of NO_x compared to the theoretically possible yield was still rather low. It ranged from 2.2% to 8.2%. The combustion of TMTM differs from the normal combustion of organic compounds. The combustion of TMTM gave hardly any unburned hydrocarbons that could be detected with the flame ionisation detector. Only when external radiation was applied some unburned hydrocarbons were detected. In line with the low content of unburned hydrocarbons, no soot could be found on the filters used for collecting soot during the experiments with TMTM.

Results are presented from three experiments with CNBA. All experiments were performed without external radiation. The phi-value was very low, below 0.25, in all experiments and the upper layer temperature reached 310°C at the most. The yields of NO_x were considerable, reaching values from 10% to 43% of the theoretically possible amount. Some unburned hydrocarbons were detected but the yields were rather low, with a highest value of 0.075g HC/g substance burned. Soot was also collected during the experiments giving yields in the area of 0.1g soot/g burned substance.

Four experiments were performed with dimethoate and in no case external radiation were applied. Dimethoate is a nitrogen containing substance and hence rather high yields of NOx were expected. However only low concentrations were detected. The yields correspond to below 1% of the yield theoretically possible. The amounts of soot collected on the sampling filters were very low. Below 0.1g soot/g burned substance was found during all the experiments with dimethoate.

Results are reported from five experiments with nylon 6,6. It was found that nylon 6,6 is rather hard to ignite with small ignition sources. As a sustained burning was needed in the experiments presented here, external radiation had to be applied. An external radiation of 22.4 kW/m^2 was used in all experiments with nylon 6,6. The external radiation gives upper layer temperatures in the area from 450°C to 600°C. A problem arose concerning the detection of CO_2 during the experiments. In most of the experiments, a concentration of CO_2 corresponding to a yield of 100% or more was detected. The reason for this has not been found in the equipment. A remaining cause might be the way in which the highest possible yield of CO_2 is calculated. One monomer unit is used when calculating the theoretical yield but it is possible that this could be done in a more relevant way.

All substances included in this work are organic substances and thus they all contain coal. After combustion, the coal can be found as soot, CO_2, CO and as unburned hydrocarbons. Other compounds can also be formed but these account for minor parts of the carbon balance. An attempt has been made to make a balance after combustion for the carbon present in the original substance. The result of these calculations are presented in table 24, where the amount of carbon lost during the experiment is compared to the amount of carbon found in the various analyses of the combustion products. As can be seen in table 24 the results vary considerably between the different substances and between different experiments with the same substance. Some conclusions can however be drawn.

For heptane, which is a simple hydrocarbon with no heteroatoms, the yield is approximately 70%.

Chlorobenzene is a substance with one chlorine atom per unit. Chlorine is or rather has often been used in chemicals with fire retardant qualities. This makes chlorobenzene a substance that is rather difficult to ignite and in the experiments without external radiation, the chlorobenzene is very close to extinction during the course of the experiment. For the experiments without external radiation, the carbon yield varies from58 to 84%. When external radiation was applied, the yields rise to 100% or more. The highest values were reached with high external radiation. Most of the carbon is found in CO_2 but the amount found as unburned hydrocarbons seems to increase when the external radiation is increased. There is an analytical problem in analysing unburned hydrocarbons containing heteroatoms since the flame ionisation meter used in the analysis is calibrated with propane. Calibration with other substances has not been made and it is not fully understood how the flame ionisation reacts when atoms like e g chlorine and sulphur are introduced.

TMTM is a substance containing nitrogen and sulphur. This substance behaves differently compared to heptane and chlorobenzene. It produces very little smoke. In fact, no smoke at all could be detected on the sampling filter. In stead, a yellow sulphur containing substance was found. Without external radiation, hardly any unburned hydrocarbons could be found and most of the recovered carbon was found as CO_2. When external radiation was applied the yield of unburned hydrocarbons increased drastically, giving total carbon yields over 100%. The problem here as with chlorobenzene is the heteroatoms giving unreliable results in the FID.

Dimethoate apart from carbon and hydrogen contains nitrogen, oxygen, phosphorus and sulphur. Most recovered carbon is found as CO_2 and only extremely small amounts of soot were detected. In one experiment, the carbon yield reaches more than 100%. The reason for this is not found.

CNBA is a hydrocarbon containing chlorine, nitrogen and oxygen. The carbon yield in the experiments with CNBA is close to 100%. Most of the carbon in the combustion gases is found in CO_2 and as soot.

Nylon 6,6 is a nitrogen-containing polymer. Since polymers react somewhat different, from other substances, when heated, it is not evident what base substance to use when calculating yields and other substance depending variables. In this report the monomer, $C_{12}H_{22}N_2O_2$ is used as the smallest unit taking part in the combustion process. This might be a simplification of the reactions involved in the combustion of nylon 6,6 and might be one reason to why the carbon yields are high, over 100%, in the main part of the experiments.

Samples of combustion gases from experiments with chlorobenzene and CNBA were analysed with ion chromatography with respect to content of HCl. GC-MS analysis was also performed in order to determine the main compounds formed during combustion of these substances. It was found that for both chlorobenzene and CNBA, a large part of the chlorine available goes into formation of HCl. 67% or more of the theoretically possible amount of HCl is formed. The dominating chlorine containing organic compound found in the GC-MS analysis is chlorobenzene. This is true both for chlorobenzene and for CNBA. In the analysis of samples from experiments with CNBA some other chlorine containing compounds were also found in so large amounts that it was possible to quantify them.

As could be expected an immense number of substances could be identified in the GC-MS analysis. Most of them could however only be identified qualitatively but for those, where it was possible a quantitative analysis was also made. The results are presented in table 20 but in short, it was found that from chlorobenzene the main compounds were unburned chlorobenzene, benzene and naphthalene. In the analysis of samples from experiments with TMTM, substances of almost the same composition as TMTM were the main compounds found. The combustion gases from dimethoate were found to contain large amounts of the solvents xylene and cyclohexanone which were used in the tested formulation. Apart from these solvents, toluene was also found in rather large quantities. The main components in the combustion gases from CNBA were chlorobenzene, naphthalene and 2-chlorobenzonitrile. Nylon 6,6 produces benzene, toluene and naphthalene as the main combustion products in the series of experiments presented here.

Table 24. Carbon recovered in gas analyses compared to carbon mass loss.

Test number	Carbon mass loss (g)	Carbon recovered (g)	Carbon Recovered (%)
HEP001	803.5	552.5	69
HEP002	1255.9	852.6	68
CB004	725.8	424.0	58
CB005	643.3	429.8	67
CB019	1309.0	947.6	72
CB020	743.4	626.9	84**
CB021	1411.7	1414.4	100
CB023	228.7	227.8	100
CB025	862.1	963.6	112
CB026	362.2	466.7	128
CB027	466.3	508.7	109
CB029	207.1	258.3	125
CB030	143.1	206.1	144
TMTM008	406.0	115.8	29*
TMTM009	419.1	187.5	45*
TMTM010	190.5	123.1	65*
TMTM014	684.4	502.8	74*
TMTM037	234.4	284.2	121*
TMTM038	370.5	462.0	125*
DIM011	786.5	291.6	37
DIM012	252.7	126.2	50
DIM013	219.2	182.8	83**
DIM015	499.6	590.2	118
CNBA017	940.9	912.5	97
CNBA018	663.8	609.8	92
NYL031	165.1	127.4	77
NYL032	112.0	121.5	109
NYL033	280.6	380.1	135
NYL034	390.8	505.1	129
NYL035	611.4	804.9	132

* The production of soot has not been included in the calculation of the carbon recovered in the gas analyses.

** The content of carbon found as unburned hydrocarbons has not been included in the calculation of carbon recovered in the gas analyses.

6 References

[1] Petersen, K. E., Markert, F. (Ed)., *Assessment of Fires in Chemical Warehouses. An Overview of the TOXFIRE Project.,* Risø National Laboratory, Roskilde Denmark, Risø-R-932, May 1999;

[2] Hietaniemi, J., Mikkola, E., *Minimising fire risks at chemical storage facilities, Basis for the guidelines for fire safety engineers,* VTT Research Notes 1811, 29 p. + app. 14 p., Espoo 1997;

[3] Särdqvist, S., *An Engineering Approach to Fire-Fighting Tactics,* Department of Fire Safety Engineering, Lund University, ISRN LUTVDG/TVBB -- 1014 -- SE, Lund 1996;

[4] Rasmussen, B., *Managing Fires in Chemical Warehouses,* Risø National Laboratory, Roskilde, Denmark, Risø-R-888 (EN), December 1996;

[5] Gunners, N.E., *Methods of Measurement and Measuring Equipment for Fire Tests*, National Swedish Institute for Materials Testing, Fire Engineering Laboratory 1967:1, 1967;

[6] Nordtest Inquiry No 1131-93, *Heat Flux Meters: Calibration*, Finland 1993;

[7] Babrauskas, V., Parker, W. J., Mulholland, G. and Twilley, W. H., *The phi-meter: A simple, fuel-independent instrument for monitoring combustion equivalence ratio,* Re. Sci. Instrum. 65 (7), July 1994;

[8] *Room Fire Test in Full Scale for Surface Products*, NORDTEST Fire Test Method, NT Fire 025;

[9] Andersson, B., Davie, F., Holmstedt, G., Kenéz, A., Särdqvist, S., *Combustion of Substances and the Impact on the Environment of the Fire Products – 1/3 Scale Room Furnace Experiments,* Department of Fire Safety Engineering, Lund University, ISRN LUTVDG/TVBB--307--SE, 1994;

[10] Babrauskas, V., Williamson, R. B., *Post-flashover Compartment Fires,* Fire Research Group, University of California, Berkeley, USA, Report No. UCB FRG 75-1, December 1975;

[11] Babrauskas, V., Grayson, S. J., *Heat Release in Fires*, Elsevier Applied Science, England 1992;

[12] Mulholland, G. W., p *2-221 - 222 in The SFPE Handbook of Fire Protection Engineering*, NFPA, 1995;

Appendix A: Detailed information from the experiments

Contents:

HEPT001

Date	960401
Substance	Heptane
Mass	1050 g
Pan diameter	20 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
14.33	Log start time
14.40	Ignition time
14.45	Start chem. sample. Flow 1.0 l/min
14.55	Stop chem. sample.
15.03	Log end time

HEPT002

Date	960410
Substance	Heptane
Mass	2218 g
Pan diameter	30 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	100 mm
	Log start time
	Ignition time
11.38	FID range changed from 500 to 1000
11.39	FID range changed from 1000 to 2000
11.41	FID range changed from 2000 to 5000
11.45	Several changes in FID range
	Test aborted due to explosion hazard
	Log end time

CB003

Date	9604010

- - Test failed - -

CB004

Date	960412
Substance	Chlorobenzene
Mass	1169 g
Pan diameter	20 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
11.56.05	Log start time
	Ignition time
12.01.33	FID range changed from 500 to 1000
12.02.16	Start soot sample. 3.1 l/min
12.07.16	Stop soot sample
12.20.28	Start chem. sample
12.25.28	Stop chem. sample
12.40.30	Log end time

The furnace was covered by a 1 cm thick soot layer after the test. Ranges possibly changed in channel 6 (NOx). Out of calibration gas M3.

CB005

Date	960412
Substance	Chlorobenzene
Mass	1026 g
Pan diameter	30 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
14.30 (appr.)	Log start time
14.36.14	Ignition time
14.48.44	FID range changed from 1000 to 5000

14.43.01	Start chem. sample. 5 min.
14.43.16	Start soot sample. 5 min. 3.2 l/min
15.05.00	Log end time

CB006

Date	960415
Substance	Chlorobenzene
Mass	
Pan diameter	40 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
appr. 14.30.	Log start time
15.06.15	Ignition time
15.11	Re-ignited
15.13	Re-ignited
15.12	FID range changed from 1000 to 5000
15.27	Log end time

FID range 1000 from start. The test was terminated due to self-choking.

TMTM007

Date	960417
Substance	TMTM
Mass	1024 g
Pan diameter	20 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
15.13	Log start time
15.14.50	Start propane burner for ignition
15.18	Stop propane burner
15.20.10	Ignition hatch closed
15.32.18	Start chem. sample
15.32.30	Start soot sample
15.39.30	Stop soot sample
15.40.00	Stop chem. sample
16.21.38	Log end time

FID range 1000 from start.

TMTM008

Date	960418
Substance	TMTM
Mass	1000 g
Pan diameter	30 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
11.23	Log start time
11.26.26	Start propane burner for ignition
11.29	Ignition
11.29.20	Stop propane burner
11.31	NOx range changed from 100 to 250
11.44.00	Start chem. sample
11.44.05	Start soot sample
11.59.40	Stop soot sample
11.59.40	Stop chem. sample
11.59	Log end time

FID range 1000 from start.

TMTM009

Date	960418
Substance	TMTM
Mass	1500 g
Pan diameter	40 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
14.31.50	Log start time
14.31.50	Start propane burner for ignition
15.34.50	Stop propane burner
15.04.35	Start chem. sample

15.25.00	Stop chem. sample. Note: 21 min
15.19.30	Log end time

Slow spread of fire in pan. FID range 1000 from start.

TMTM010

Date	960419
Substance	TMTM
Mass	2164 g
Pan diameter	40 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
14.30.41	Log start time
14.36.22	Start propane burner for ignition
14.39.15	Stop propane burner
14.46.08	Start chem. sample
14.53.46	Start chem. sample. Note: 21 min
15.11.57	Log end time

Ring burner output 15 kW. Bluish-white flames at 14.53. All yellow flames at 15.04.

DIM011

Date	960429
Substance	Cyclohexanone 77% Xylene 23%
Mass	1000 g
Pan diameter	20 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
18...	Log start time
18.31.04	Ignition
18.38.24	Start chem. sample
18.45.31	Stop chem. sample. 1 l/min
15.11.57	Log end time

Pre-test with solvents in dimethoate solution.

DIM012

Date	960429
Substance	Cyclohexanone 442.5 g, Xylene 132.5 g, Dimethoate, 44.6 g, Emulgator 5.4 g,
Mass	511 g solver from previous test + 114 g dimethoate solution = 625 g
Pan diameter	20 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
20.37.07	Log start time
20.42.17	Start chem. sample
20.42.28	Start soot sample
20.47.17	Stop chem. sample
20.47.28	Stop soot sample
21.06.47	Log end time

DIM013

Date	960430
Substance	Cyclohexanone 442.5 g, Xylene 132.5 g, Dimethoate, 44.6 g, Emulgator 5.4 g,
Mass	511 g solver from test DIM011 + 114 g dimethoate solution = 625 g
Pan diameter	30 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
09.43.07	Log start time
09.45.24	Ignition
09.50.14	Start soot sample
09.50.26	Start chem. sample
09.55.06	Stop soot sample

09.55.54	Stop chem. sample
09.56.57	Start extra chem. sample
10.00.15	Stop chem. sample. (After extinction)
10.01.31	Log end time

TMTM014

Date	960514
Substance	TMTM
Mass	2000 g
Pan diameter	40 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
11.04.26	Log start time
11.05.13	Start propane burner for ignition
11.07.00	Stop propane burner
11.19.42	Start wet chem. sample 1 l/min
11.19.57	Start soot sample. 3.1 l/min
11.24.43	Stop wet chem. sample
11.26.13	Start chem. sample 1 l/min
11.29.57	Stop soot sample
11.31.13	Stop chem. sample
11.37.33	Log end time

DIM015

Date	960514
Substance	Cyclohexanone 858 g, Xylene 282 g, Dimethoate, 98 g, Emulgator 12 g,
Mass	750 g cyclohexanone + 250 g xylene + 250 g dimethoate solution = 1250 g
Pan diameter	30 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
15.00.05	Log start time
15.01.43	Start propane burner for ignition
15.02.07	Stop propane burner
15.06.40	Start wet chem. sample
15.07.00	Start soot sample
15.12.00	Stop wet chem. sample
15.13.23	Start chem. sample
15.13.34	Stop soot sample
15.18.44	Stop chem. sample
15.24	Log end time

About 2-3 ml of a very evil smelling liquid left in pan after the test.

CNBA016

Date	960515
Substance	CNBA
Mass	1087 g
Pan diameter	20 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
09.29.29	Log start time
09.33.28	Start propane burner for ignition
09.35.05	Stop propane burner
09.35.53	Start propane burner
09.37.23	Stop propane burner
09.39.43	Start propane burner
09.41.41	Stop propane burner
09.42.04	Start propane burner
09.45.12	Stop propane burner
09.47.00	Log end time

Test terminated. Didn’t burn

CNBA017

Date	960515
Substance	CNBA

Mass	2460 g
Pan diameter	30 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
11.01.56	Log start time
11.06.26	Start propane burner for ignition
11.12.10	Stop propane burner
11.12.40	Ignition hatch closed
11.18.20	Start wet chem. sample
11.18.33	Start soot sample. Failed
appr. 11.21	Self extinction
11.21.58	Stop wet chem. sample. Failed.
11.26.24	Start propane burner
11.28.37	Start propane burner
11.32.45	Start chem. sample
11.36.38	Stop chem. sample
11.36.50	Self extinction
11.39.50	Start propane burner
11.46	Log end time

Test terminated.

CNBA018

Date	960515
Substance	CNBA and Polypropylene (non woven)
Mass	2478 g CNBA + 222 g PP
Pan diameter	30 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
15.11.02	Log start time
15.41.46	Start propane burner for ignition
15.47.48	Stop propane burner
15.48.15	Ignition hatch closed
15.50.22	Start wet chem. sample
15.50.32	Start soot sample
15.52.26	Stop wet chem. sample
15.53.05	Stop soot sample
15.54.06	Start chem. sample
15.56.15	Stop chem. sample
16.09.00	Ignition hatch open
16.09.20	Hatch closed
16.11	Self extinction
16.12.31	Start propane burner
16.15.07	Stop propane burner
16.21.35	Log end time

Log channel 17 (load cell) show 5 kg. Check did not give any clue.

CB019

Date	960521
Substance	Chlorobenzene
Mass	2041 g
Pan diameter	20 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	70 mm
13.56.40	Log start time
14.07.20	Ignition
14.10.00	FID range changed from 500 to 2000
14.17.42	Start wet chem. sample
14.17.53	Start soot sample
14.20.19	Stop soot sample
14.23.03	Stop wet chem. sample
14.24.11	Start chem. sample
14.29.11	Stop chem. sample
14.42.52	Log end time

No NOx measurements.

CB020

Date	960603
Substance	Chlorobenzene
Mass	2514 g
Pan diameter	20 cm
Air inlet	width 45 cm, height 20 cm
Duct diameter	30 mm
appr. 15.35	Log start time
15.41.40	Ignition
15.42.30	FID range changed from 500 to 5000
15.43.15	Duct changed from 30 mm to 50 mm
16.03.19	Duct changed from 50 mm to 60 mm
16.11.16	Log end time

No NOx measurements. Runtime error in computer during the test. A couple of minutes delay, then restart of computer. Computer files ..020 and ..020B.

CB021

Date	960607
Substance	Chlorobenzene
Mass	2312 g
Pan diameter	20 cm
Air inlet	width 45 cm, height 20 cm
Furnace temp.	appr. 250 °C
Duct diameter	70 mm
14.18.18	Log start time
	Ignition
14.19.50	Duct changed from 70 mm to 50 mm

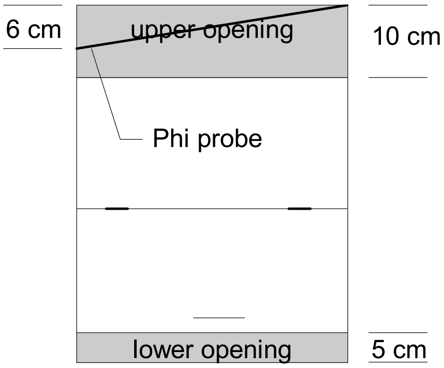
No NOx measurements. FID range 5000.

Test emergency terminated. Flow reducer in duct removed. Ignition hatch partly opened.

CB022

Date	960612
Substance	Chlorobenzene
Mass	678 g
Pan diameter	10 cm
Air inlet	width 45 cm, height: see below
Furnace temp.	appr. 250 °C
Duct diameter	70 mm
10.45.18	Log start time
10.48.40	Ignition
10.55.08	Start wet chem. sample
10.56.02	Start soot sample
11.00.02	Stop wet chem. sample
11.00.02	Stop soot sample
11.40.18	Log end time

Opening modified:



No NOx measurements. FID range 5000.

CB023

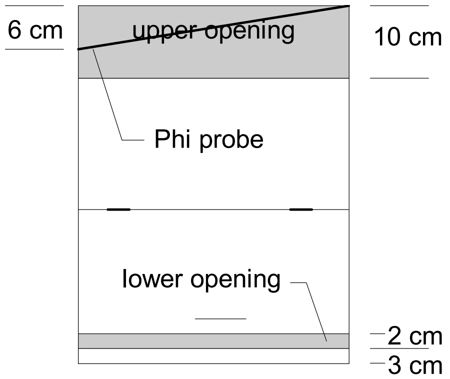
Date	960612
Substance	Chlorobenzene
Mass	356
Pan diameter	10 cm
Air inlet	width 45 cm, height: see below

Furnace temp. appr. 250 °C

Duct diameter 30 mm

14.06.30	Log start time
14.10.21	Ignition
14.24.29	Start chem. sample
14.25.40	Start soot sample. 0.9 l/min
14.29.29	Stop chem. sample
14.25.41	Stop soot sample
14.27-14.31	Phi probe cleaned by back blowing.
14.45.20	Log end time

Opening modified:



No NOx measurements. FID range 5000. Phi meter smoke logged during end of test?

CB024

Date	960612
Substance	Chlorobenzene
Mass	463
Pan diameter	15 cm
Air inlet	as in CB023

Furnace temp. appr. 250 °C

Duct diameter 30 mm

15.47.26	Log start time
15.49.08	Ignition
15.57.54	Phi = 40
16.09.59	Log end time

No NOx measurements. FID range 5000. No calibration made after test.

CB025

Date	960614
Substance	Chlorobenzene
Mass	1426 g
Pan diameter	20 cm
Air inlet	width 45 cm, height 10 cm (upper) + 2 cm (lower)

Furnace temp. appr. 260 °C

Duct diameter 40 mm

14.58.00	Log start time
15.00.37	Ignition
15.03.10	Duct changed from 40 mm to 60 mm
15.10.43	Start wet chem. sample
15.11.33	Start soot sample
15.15.39	Stop wet chem. sample
15.15.50	Stop soot sample
15.15.55	Duct changed from 60 mm to 70 mm
15.16.30	Duct changed from 70 mm to 90 mm
15.28.30	Log end time

No NOx measurements. FID range 5000.

CB026

Date	960618
Substance	Chlorobenzene
Mass	614 g
Pan diameter	10 cm
Air inlet	width 45 cm, height 10 cm (upper) + 2 cm (lower)
Furnace temp. appr.	520 °C
Duct diameter	50 mm
09.24.30	Log start time
09.31.04	Ignition
09.35.57	Duct changed from 50 mm to 70 mm
09.44.53	Log end time

No NOx measurements. FID range 5000.

CB027

Date	960618
Substance	Chlorobenzene
Mass	812 g
Pan diameter	15 cm
Air inlet	width 45 cm, height 10 cm (upper) + 2 cm (lower)
Furnace temp. appr.	520 °C
Duct diameter	70 mm
11.36.50	Log start time
11.42.36	Ignition
11.47.17	Duct changed from 70 mm to 90 mm
11.56.00	Log end time

No NOx measurements. FID range 5000.

CB028

Date	960619
Substance	Chlorobenzene
Mass	1045 g
Pan diameter	15 cm
Air inlet	width 45 cm, height 10 cm (upper) + 1 cm (lower)
Furnace temp. appr.	520 °C
Duct diameter	70 mm
14.13.00	Log start time
14.15.25	Ignition
14.19.22	Duct flow reducer removed. Extinction soon after
14.27	Log end time

Chlorobenzene spilled in furnace at ignition

FID range 5000.

CB029

Date	960619
Substance	Chlorobenzene
Mass	371 g
Pan diameter	10 cm
Air inlet	width 45 cm, height 10 cm (upper) + 1 cm (lower)
Furnace temp. appr.	520 °C
Duct diameter	70 mm
14.35.05	Log start time
14.36.35	Ignition
14.48.50	Log end time

FID range 5000. Calibration: see CB028

CB030

Date	960619
Substance	Chlorobenzene
Mass	289 g
Pan diameter	15 cm
Air inlet	width 45 cm, height 10 cm (upper) + 1 cm (lower)
Furnace temp. appr.	520 °C
Duct diameter	70 mm

14.53.00	Log start time
14.55.20	Ignition
15.03.25	Log end time

FID range 5000. Calibration: see CB028

NY031

Date	960620
Substance	Nylon
Mass	434 g
Pan diameter	10 cm
Air inlet	width 45 cm, height 10 cm (upper) + 1 cm (lower)

Furnace temp. appr. 500 °C

Duct diameter 70 mm

10.42.00	Log start time
10.43.30	Material placed on load cell
10.54	Ignition
11.02.52	Duct changed from 70 mm to 30 mm
11.51	Log end time.

NOx range 1000. FID range 1000. Test terminated at 11.51: gave no more data of interest.

NY032

Date	960620
Substance	Nylon
Mass	494 g
Pan diameter	15 cm
Air inlet	width 45 cm, height 10 cm (upper) + 1 cm (lower)

Furnace temp. appr. 520 °C

Duct diameter 30 mm

11.57.30	Log start time
11.58.30	Material placed on load cell
12.02.45	Duct changed from 30 mm to 40 mm
12.05.30	Start propane burner for ignition
12.06.30	Ignition. Stop propane burner
12.19.00-12.21.30	Cleaning the O2-CO2-CO meter
12.23.23	Start wet chem. sample
12.24.20	Start soot sample
12.30.10	Stop wet chem. sample
12.30.20	Stop soot sample
12.31.53	Start chem. sample
12.37.10	Stop chem. sample
12.42.30-12.44.00	Cleaning the O2-CO2-CO meter
12.49	Self extinction
12.56.14	Log end time.

NOx range 1000. FID range 1000.

NY033

Date	960624
Substance	Nylon
Mass	560 g
Pan diameter	20 cm
Air inlet	width 45 cm, height 10 cm (upper) + 1 cm (lower)

Furnace temp. appr. 520 °C

Duct diameter 40 mm

14.36.30	Log start time
	Material placed on load cell
14.39.30	Ignition
14.42.20	Duct changed from 40 mm to 60 mm
appr. 14.45	Boiled-over material almost burnt up.
14.48.38	Duct changed from 60 mm to 40 mm
14.55.10	Start soot sample
14.57.45	Stop soot sample. Fire out

15.00.37	Log end time.

The material melted and boiled over the pan, thus making the burning diameter larger.

NOx range 1000. FID range 500. Load cell may be out of function, due to lack of cooling water during the weekend.

NY034

Date	960625
Substance	Nylon
Mass	700 g
Pan diameter	30 cm
Air inlet	width 45 cm, height 10 cm (upper) + 1 cm (lower)

Furnace temp. appr. 520 °C

Duct diameter 40 mm

appr. 10.40	Material placed on load cell for melting
11.05.30	Log start time
11.11.08	Ignition
11.16.28	Start soot sample
11.21.19	Stop soot sample
11.21.42	Start wet chem. sample
11.23.42	Stop wet chem. sample
11.24.25	Start chem. sample
11.26.24	Stop chem. sample
11.42	Log end time.

NOx range 1000. FID range 1000. NOx meter smoke logged?

NY035

Date	960625
Substance	Nylon
Mass	1000 g
Pan diameter	40 cm
Air inlet	width 45 cm, height 10 cm (upper) + 1 cm (lower)

Furnace temp. appr. 520 °C

Duct diameter 40 mm

14.53	Material placed on load cell for melting
15.09.00	Log start time
15.10.20	Ignition
15.20.12	Start soot sample
15.25.00	Stop soot sample
15.17.35	Start wet chem. sample
15.18.20	Duct changed from 40 mm to 60 mm
15.20.00	Stop wet chem. sample
15.21.50	NOx meter tested with calibration gas. Conclusion: out of order.
15.23.04 - 15.23.24	NOx meter measuring only NO.
15.29.20	Log end time.

NOx range 1000. FID range 1000.

NY036

Date	960627
Substance	Nylon
Mass	1300 g
Pan diameter	40 cm
Air inlet	width 45 cm, height 10 cm (upper) + 0 cm (lower)

Furnace temp. appr. 520 °C

Duct diameter 50 mm

10.54.00	Material placed on load cell for melting
appr. 11.09.30	Spontaneous ignition
appr. 11.09.30	Log start time
11.18.48	Start wet chem. sample
11.20.48	Stop wet chem. sample
11.23.13	Start chem. sample

11.27.13	Stop chem. sample
11.22.50	Duct changed from 50 mm to 60 mm
11.40.00	Log end time.

NOx range 1000. FID range 1000. NOx meter OK?

TMTM037

Date	960627
Substance	TMTM
Mass	700 g
Pan diameter	30 cm
Air inlet	width 45 cm, height 10 cm (upper) + 1 cm (lower)

Furnace temp. appr. 520 °C

Duct diameter 60 mm

13.48.40	Log start time
appr. 13.50	Material placed on load cell for melting
appr. 13.52	Spontaneous ignition
13.55	Bluish white flames
13.58	Brown flames
13.59.42	Start wet chem. sample
14.00	Yellow flames
14.01.42	Stop wet chem. sample
14.03.25	Log end time.

NOx range 1000. FID range 1000. NOx meter OK?

TMTM038

Date	960627
Substance	TMTM
Mass	1100 g
Pan diameter	30 cm
Air inlet	width 45 cm, height 10 cm (upper) + 1 cm (lower)

Furnace temp. appr. 520 °C

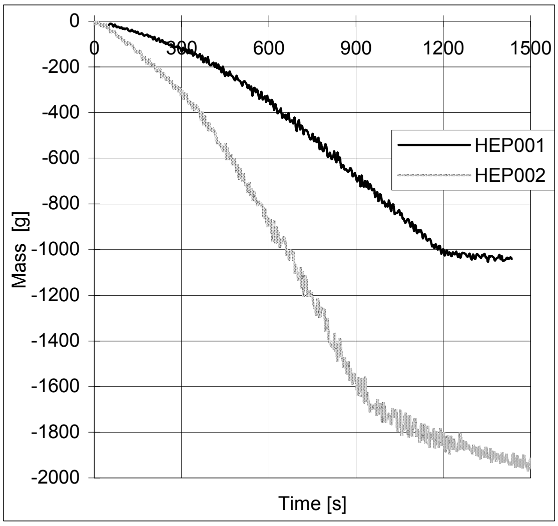
Duct diameter 60 mm

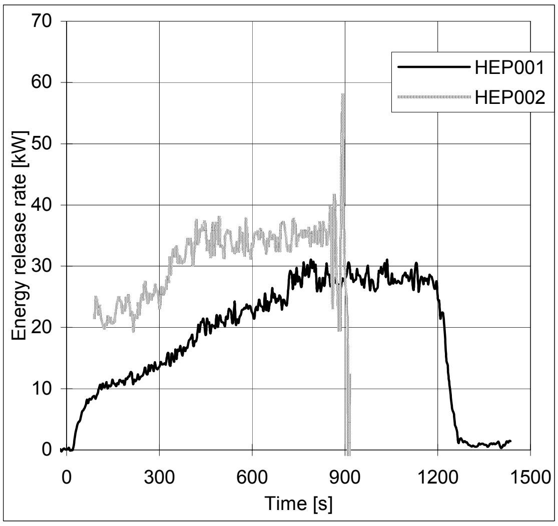
14.32.21	Log start time
14.32.45	Pan placed on load cell
14.35	Not possible to ignite with propane burner
14.36.20	Spontaneous ignition

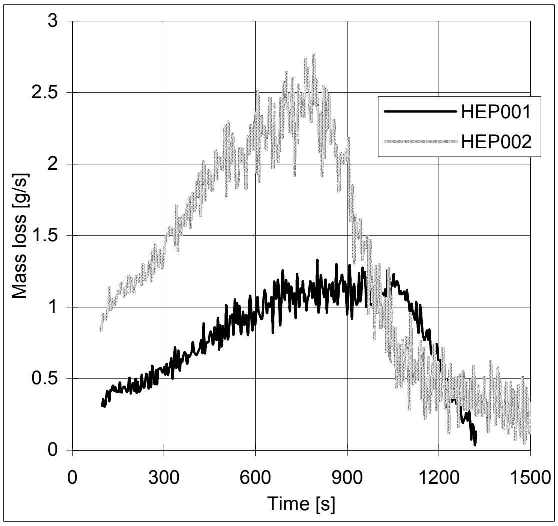
14.43.02	Start wet chem. sample
14.43.50	Duct changed from 60 mm to 70 mm
14.47.30	Stop wet chem. sample
14.03.25	Log end time.

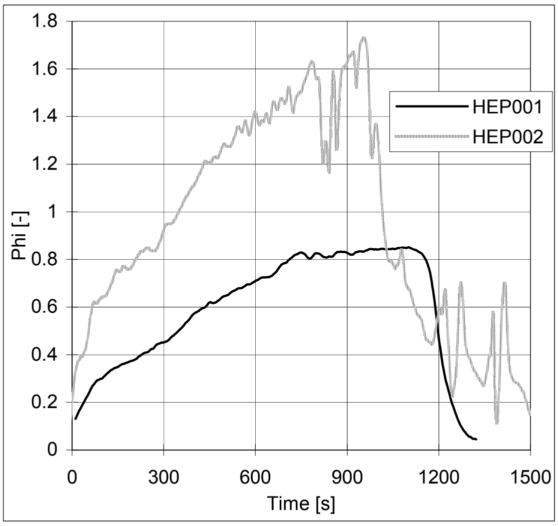
NOx range 1000. FID range 1000. Test similar to TMTM037 but having larger mass.

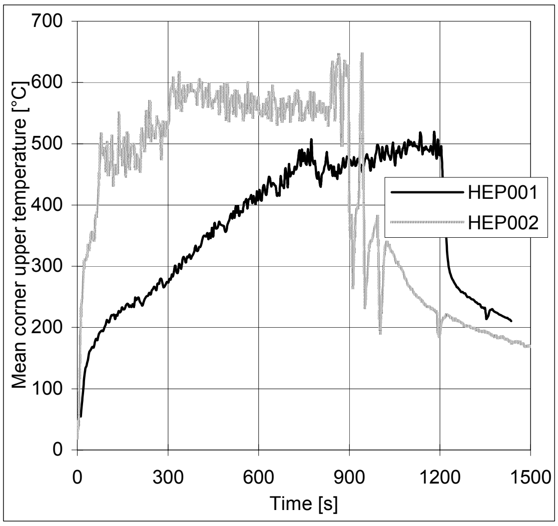
Appendix:Heptane

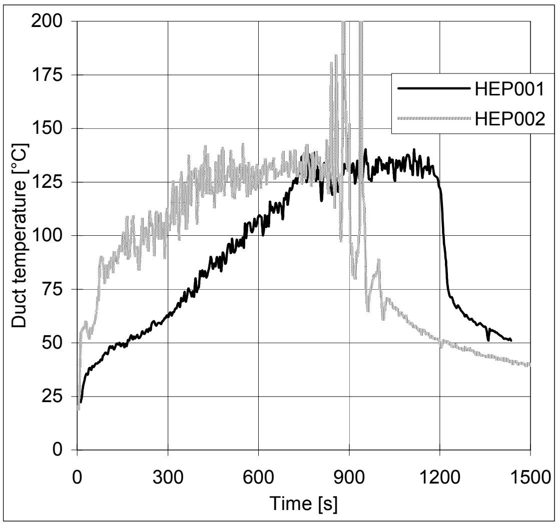




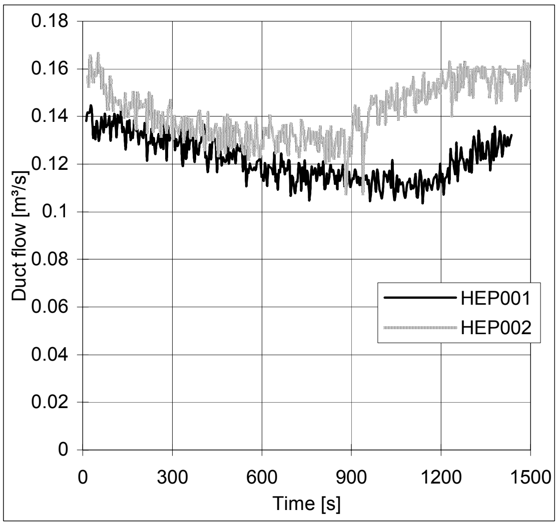


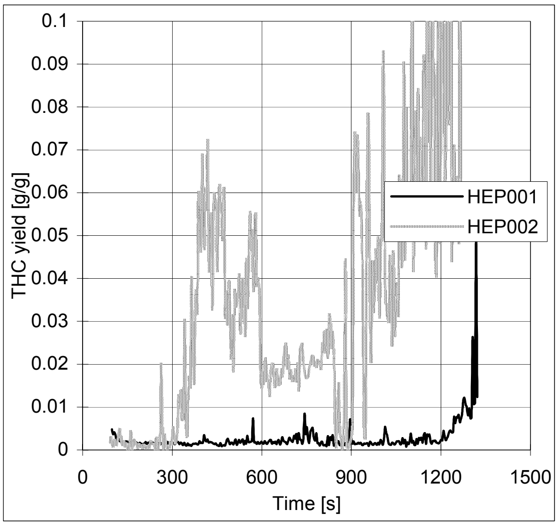


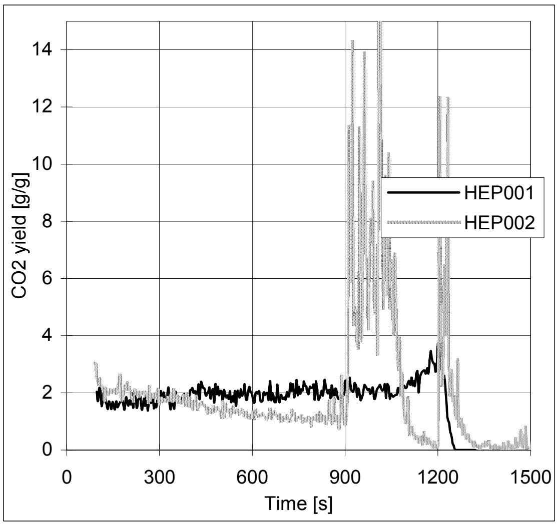


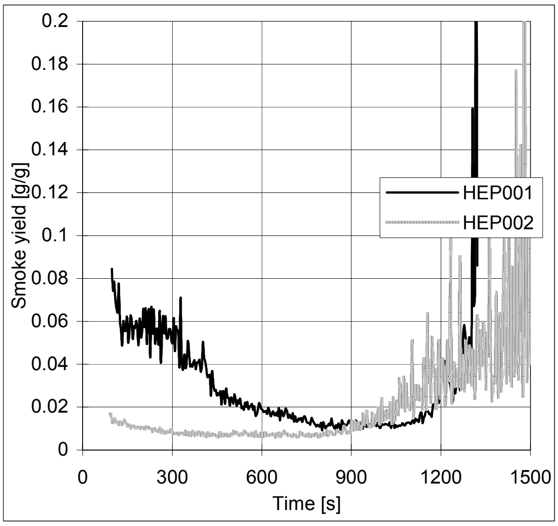


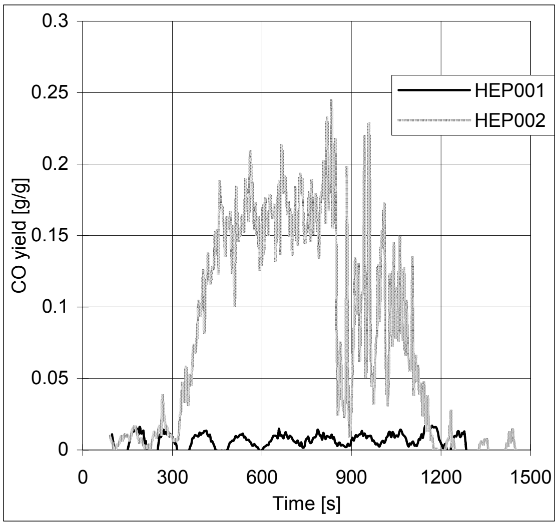
Appendix:Heptane

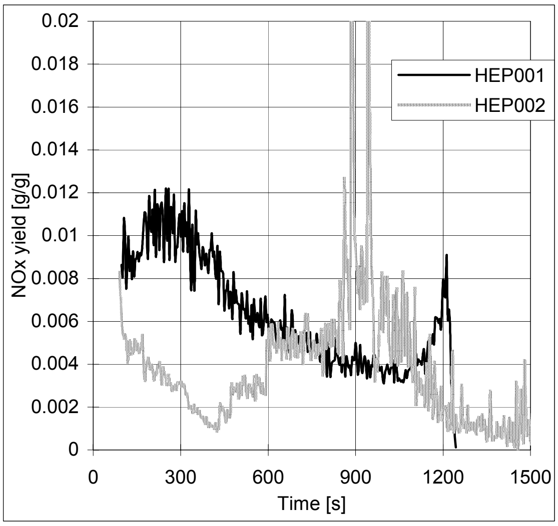




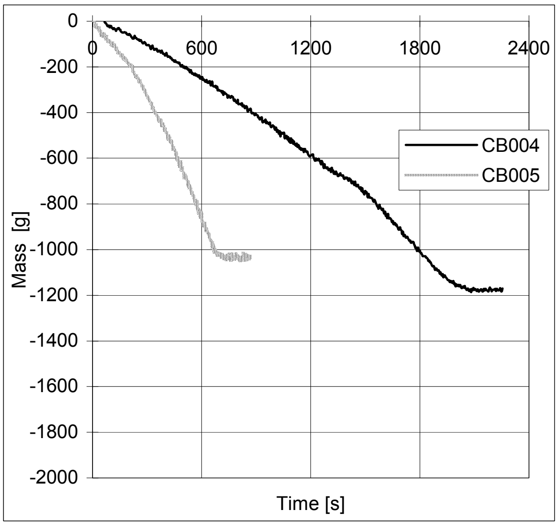


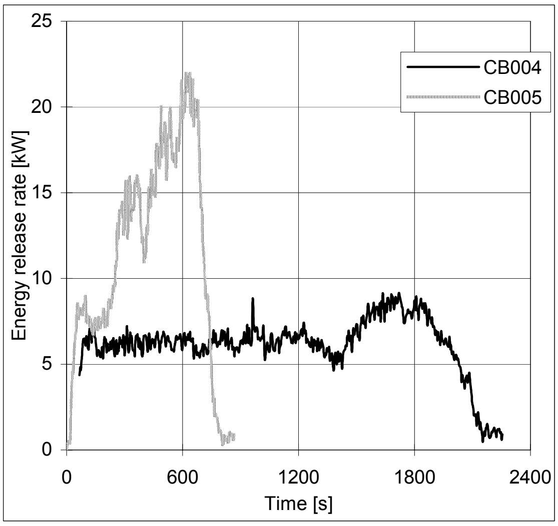


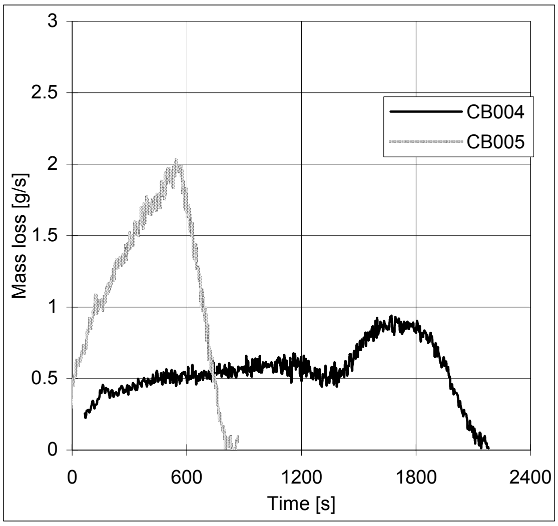


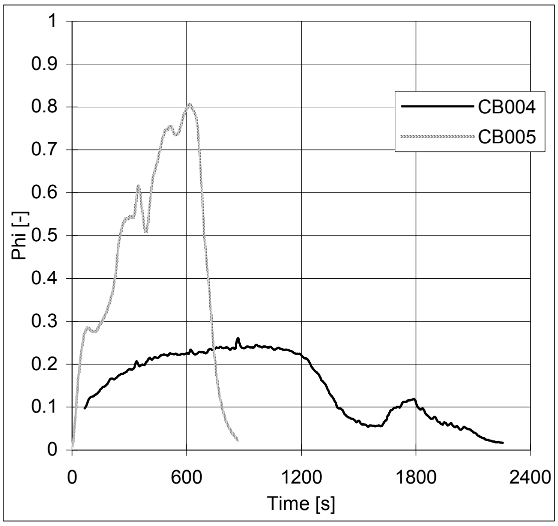


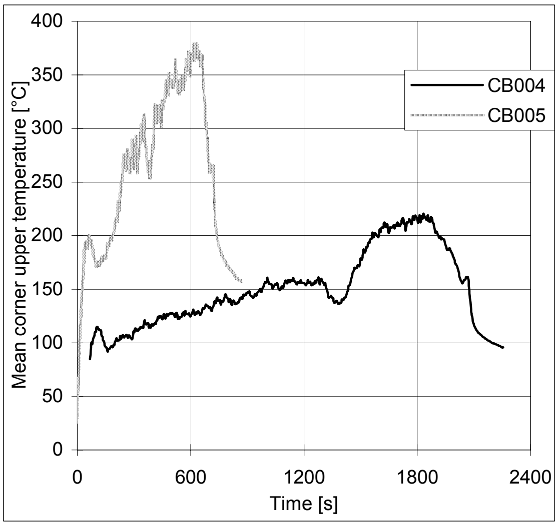
Appendix:Chlorobenzene

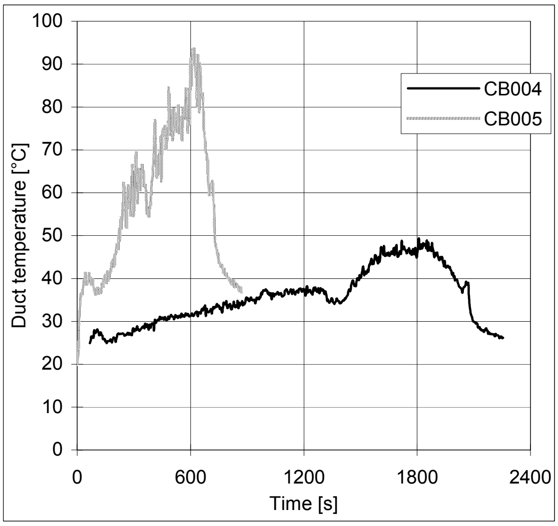




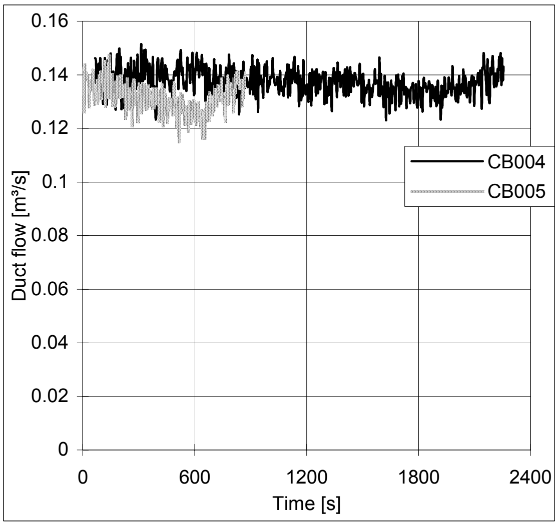


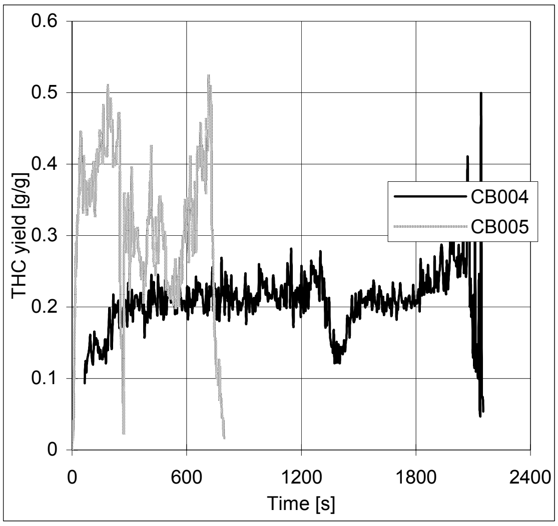


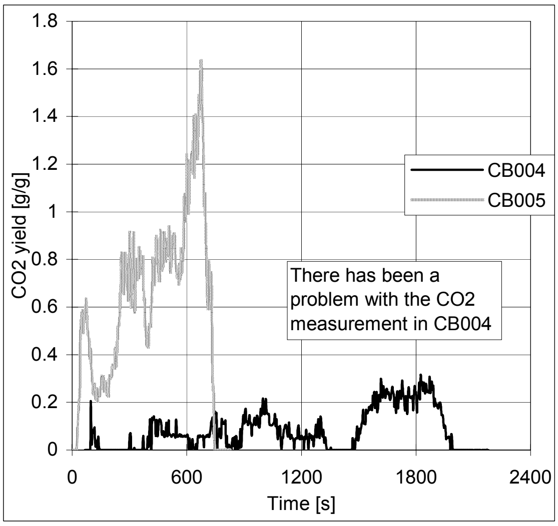


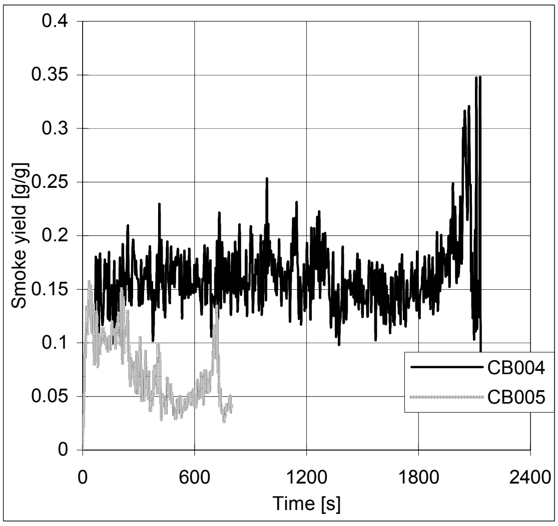


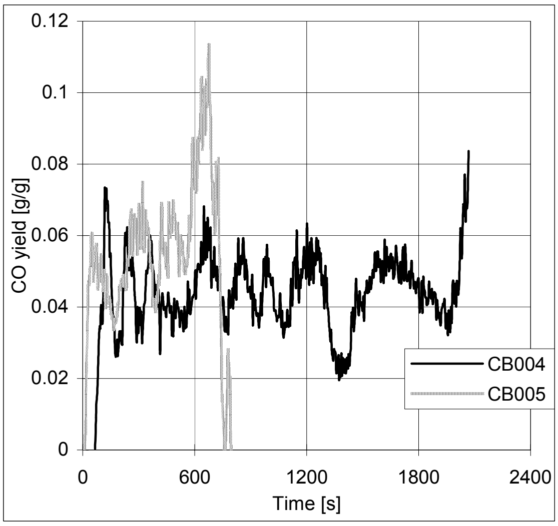
Appendix:Chlorobenzene

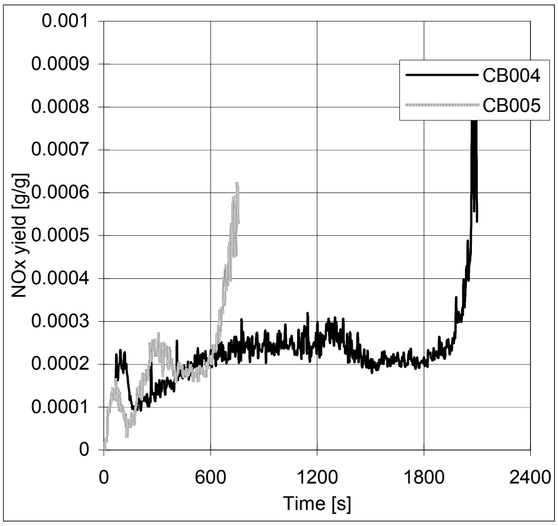




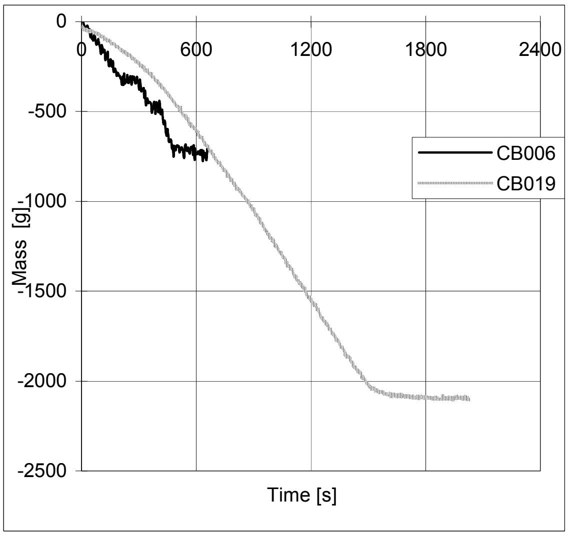


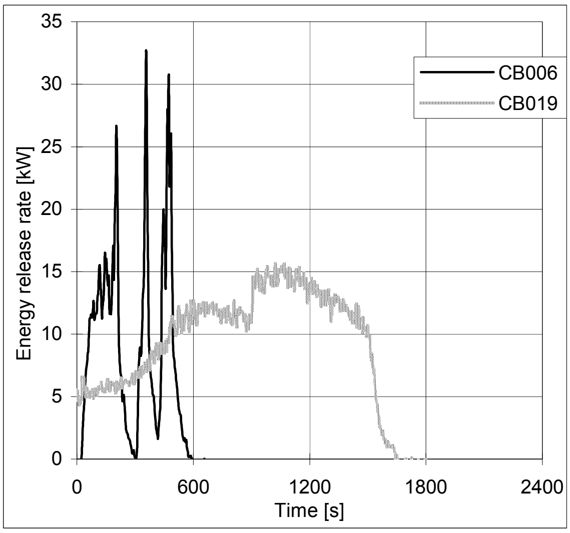


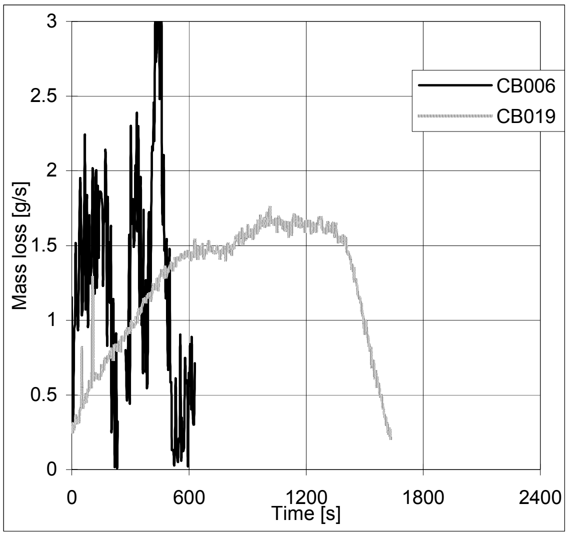


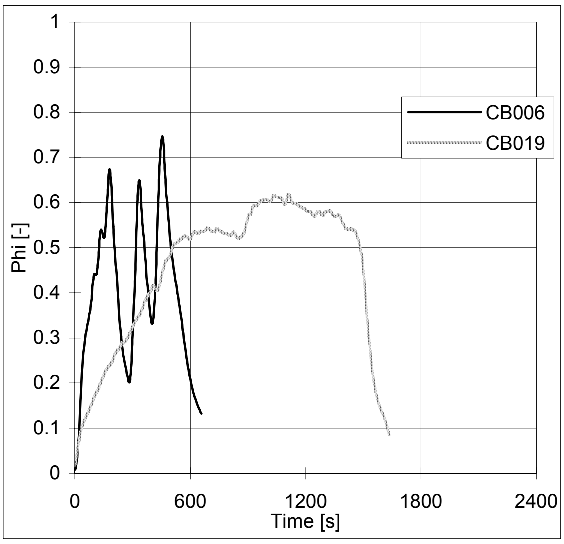


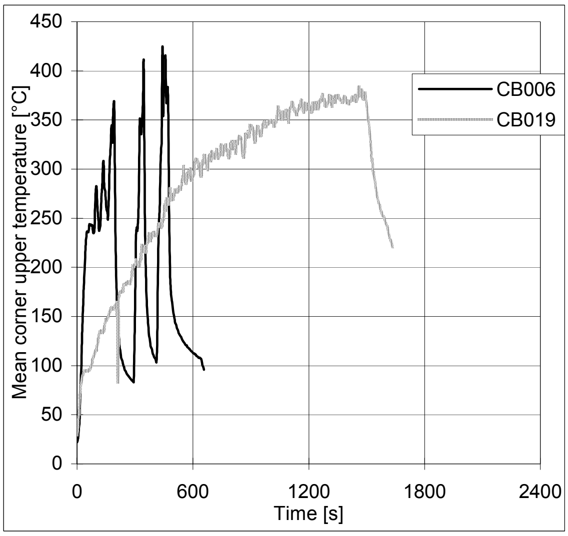
Appendix:Chlorobenzene

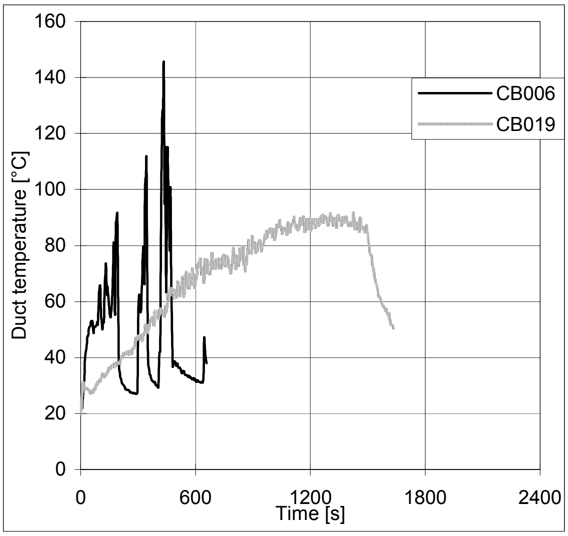




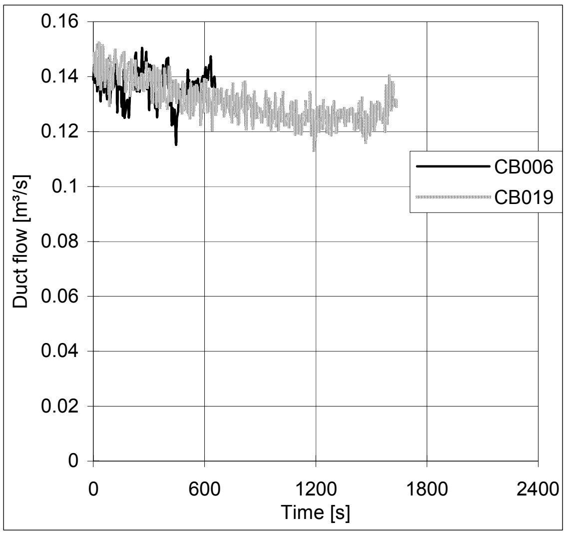


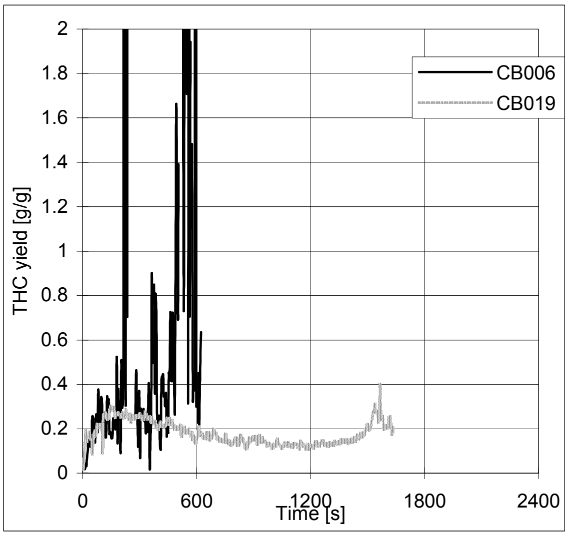


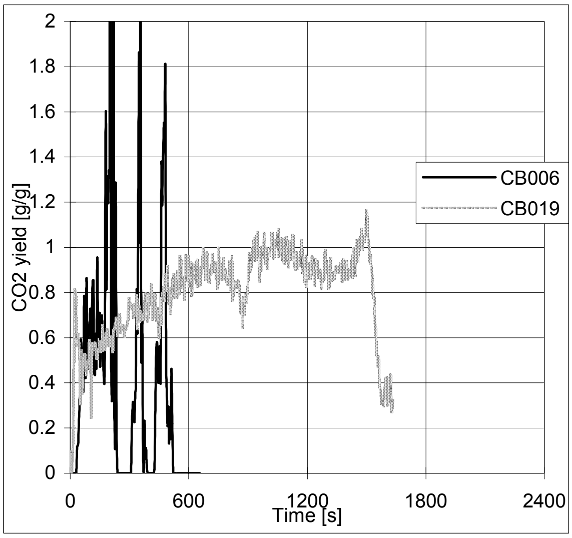


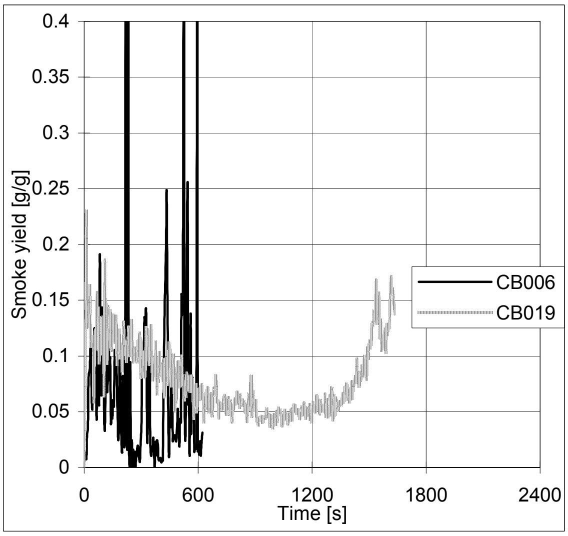


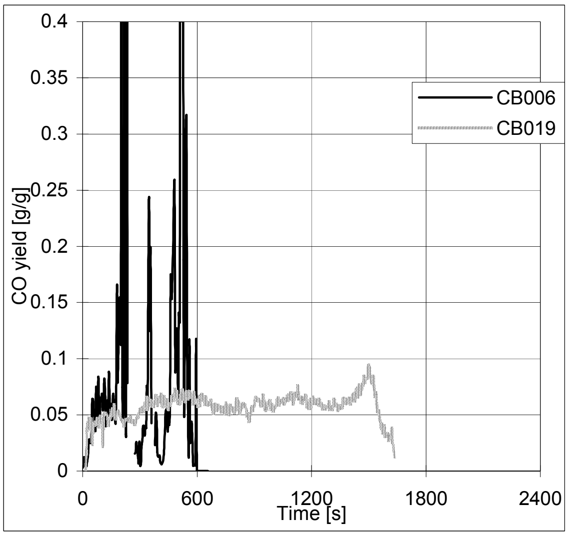
Appendix:Chlorobenzene





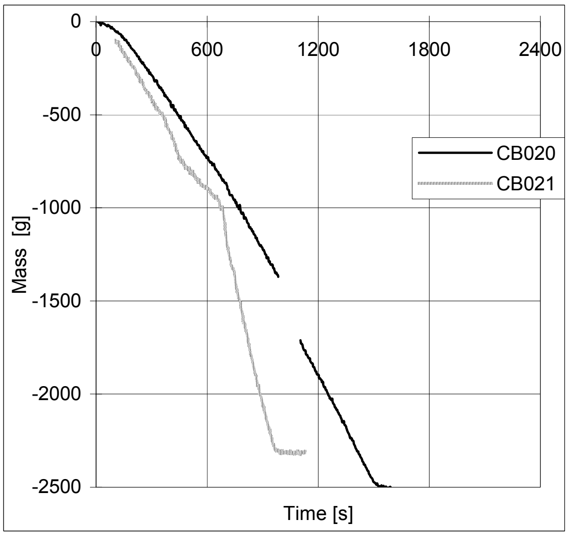


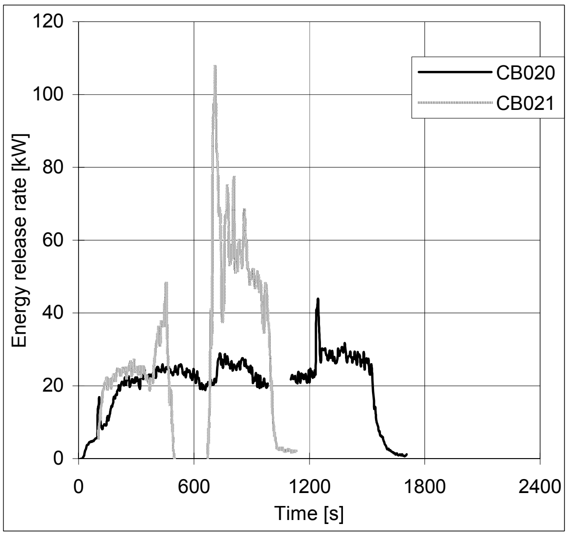


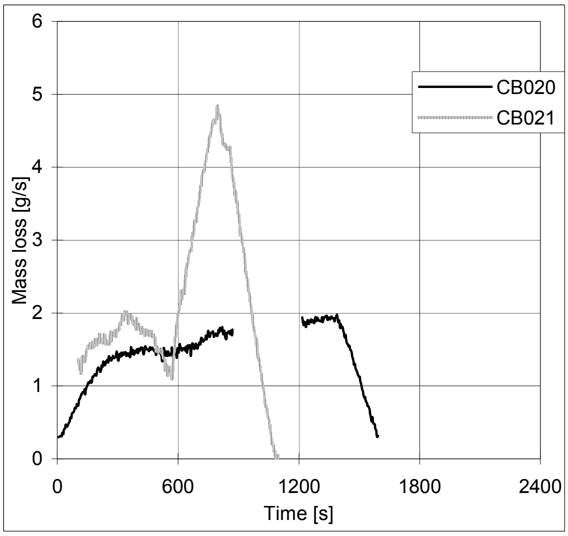


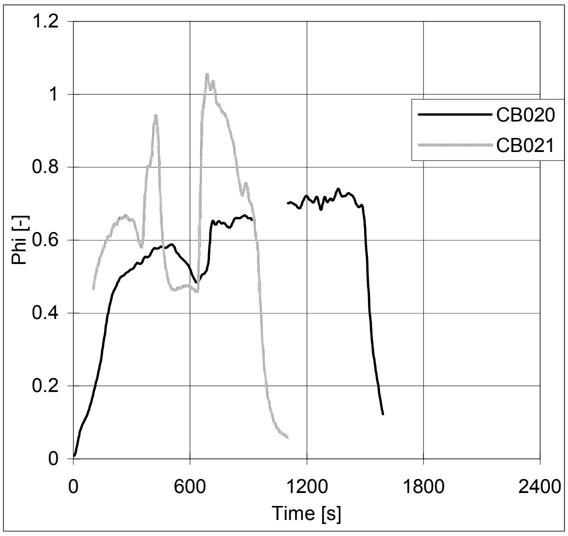
The NOx production
was not measured
during these tests.

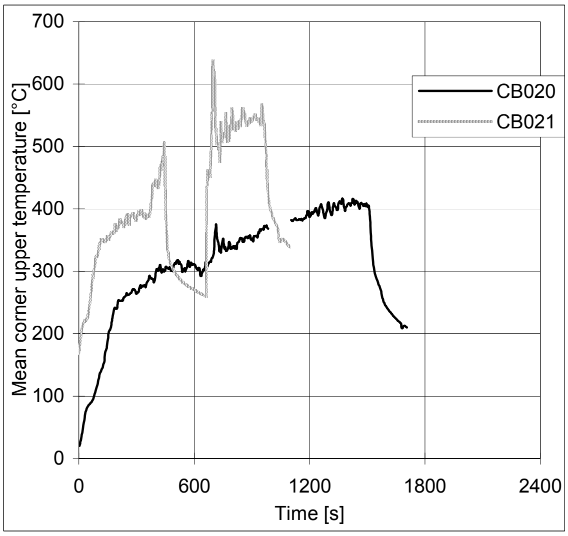
Appendix:Chlorobenzene

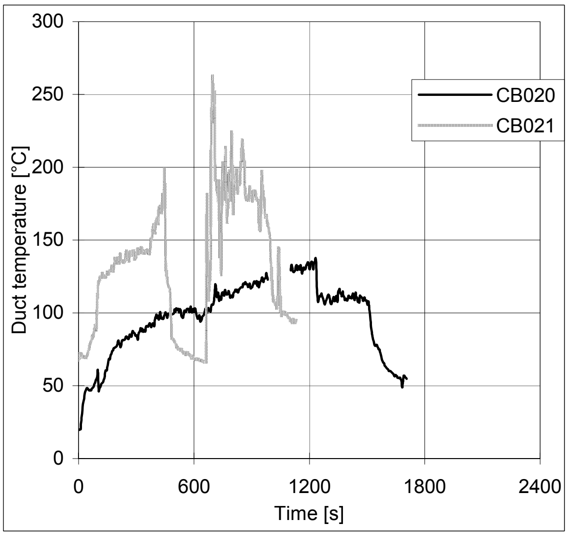


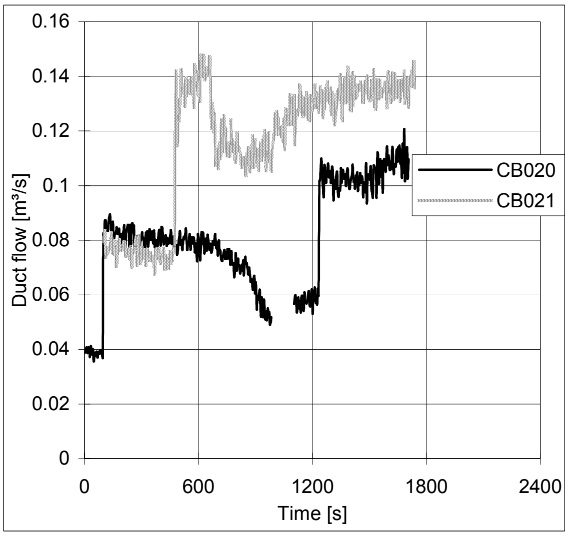


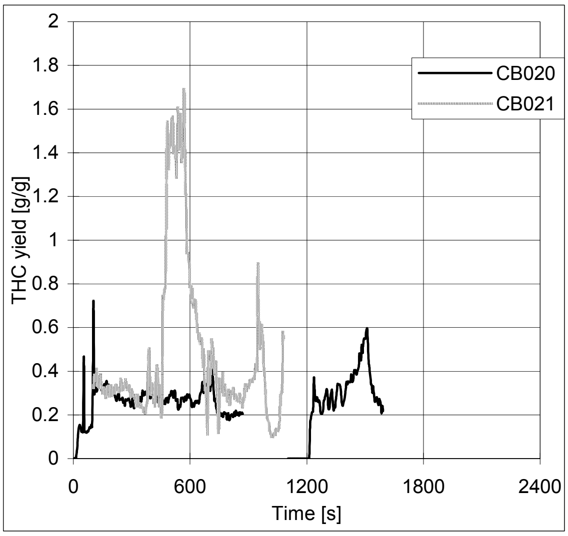


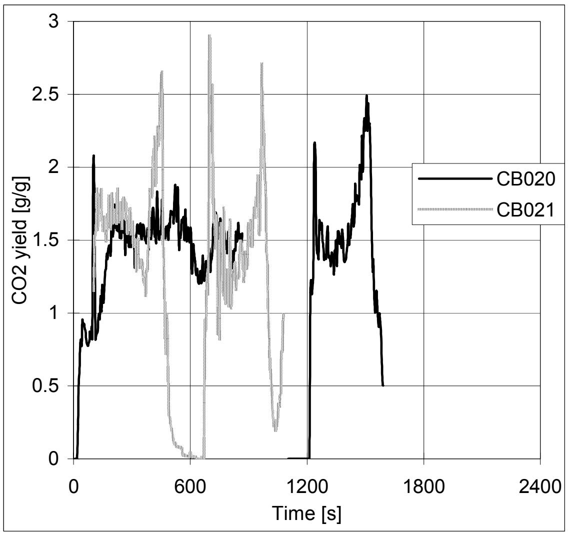


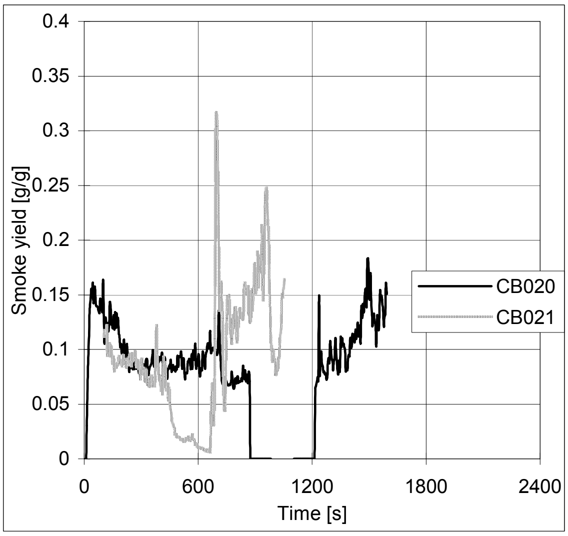


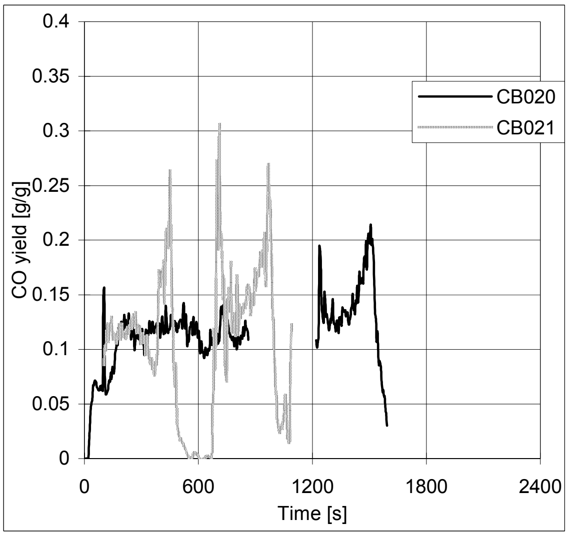




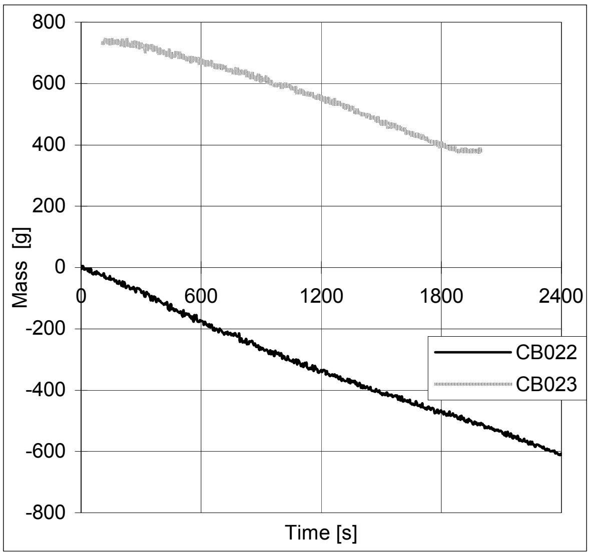


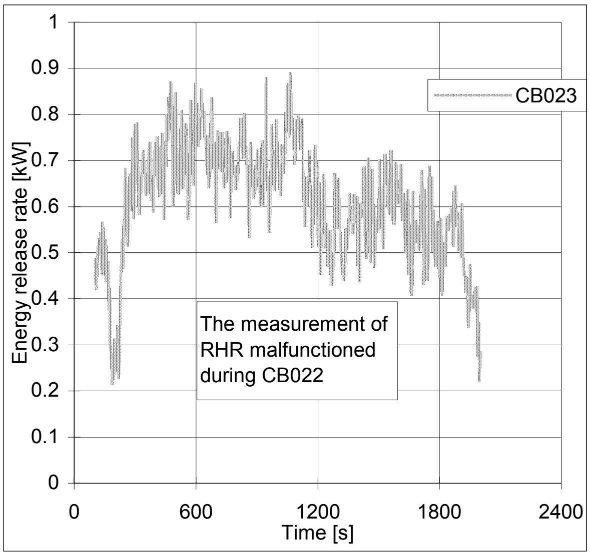




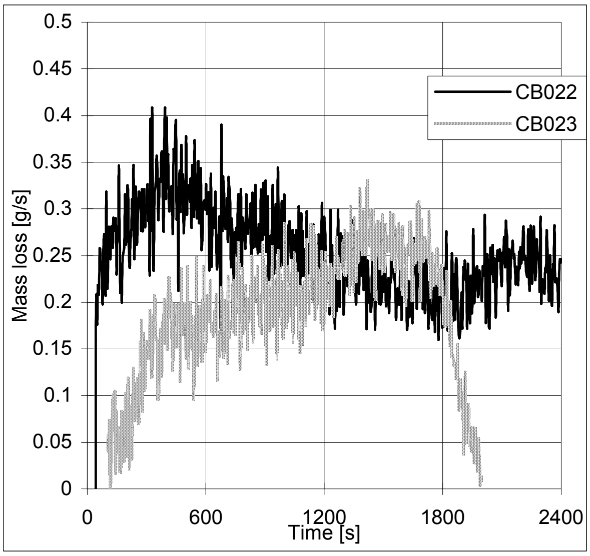


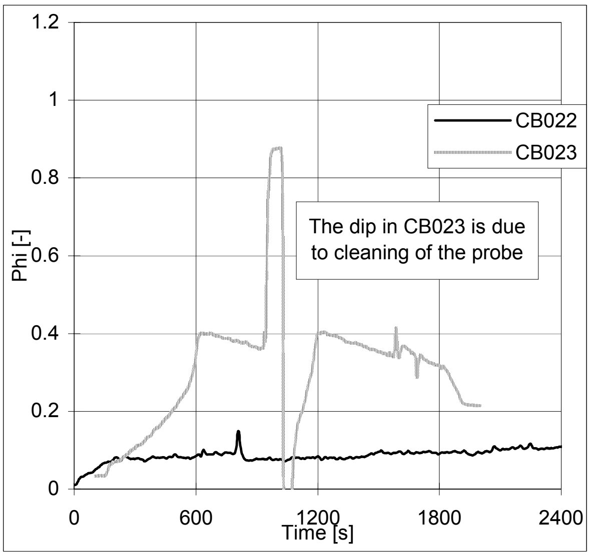
The NOx production
was not measured
during these tests.



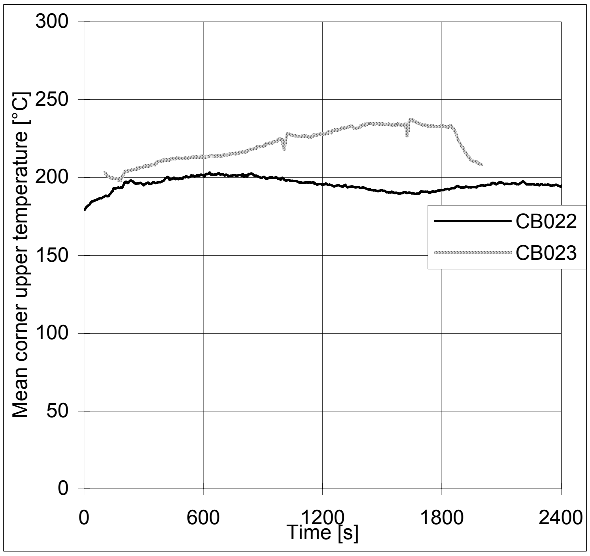


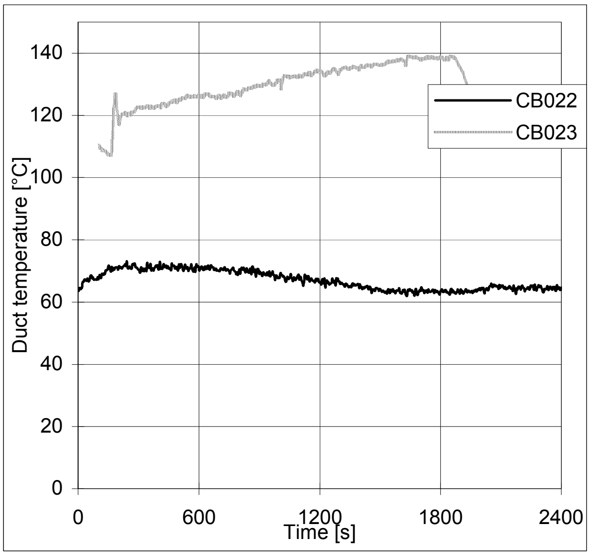
The measurement of RHR malfunctioned during CB022

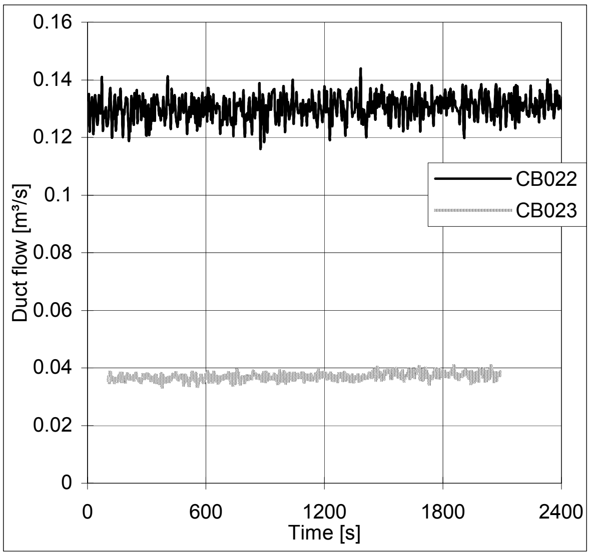


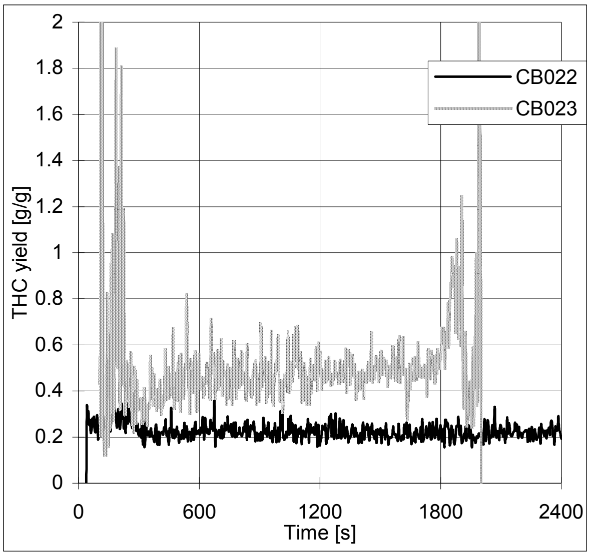


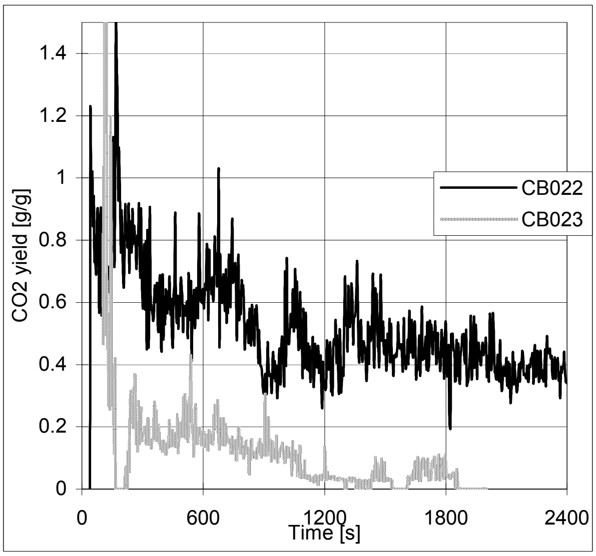
The dip in CB023 is due to cleaning of the probe

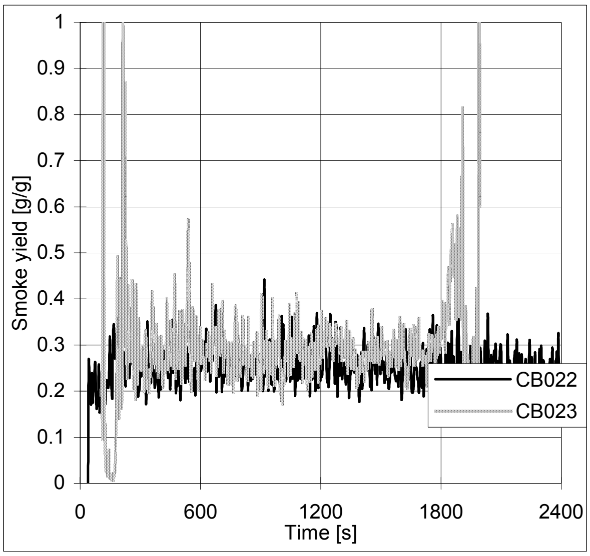


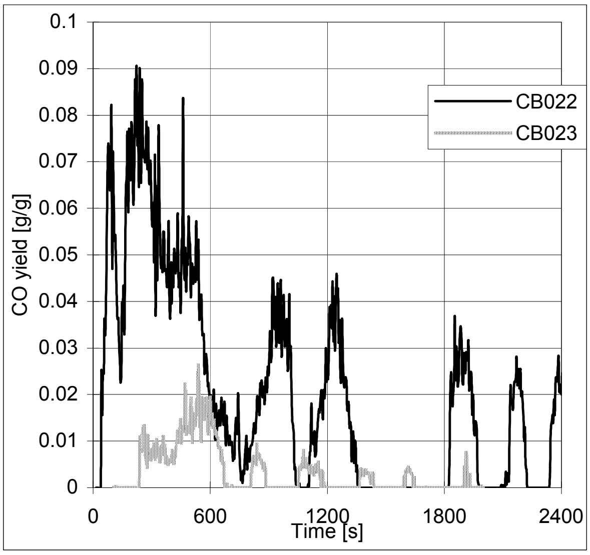






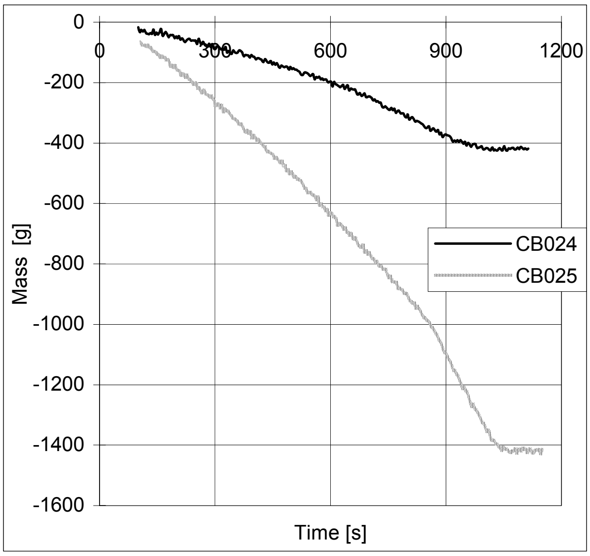


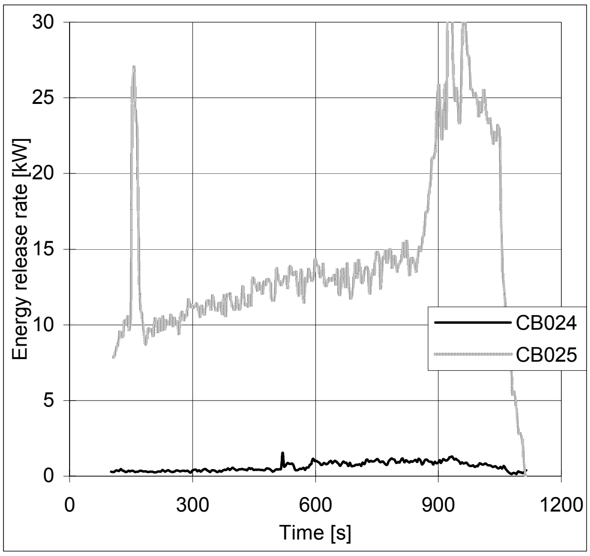


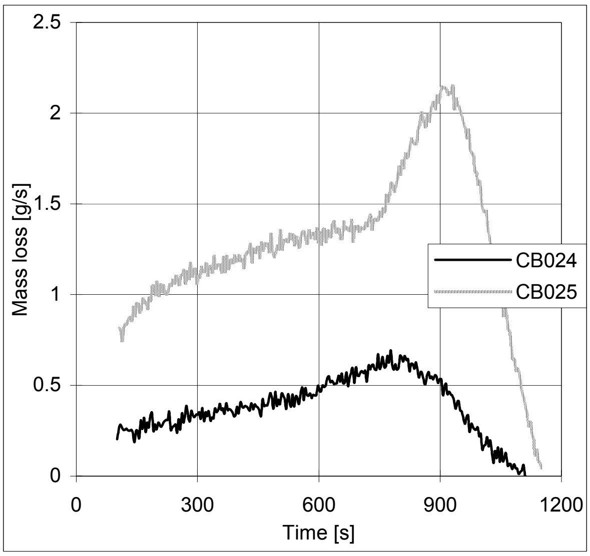


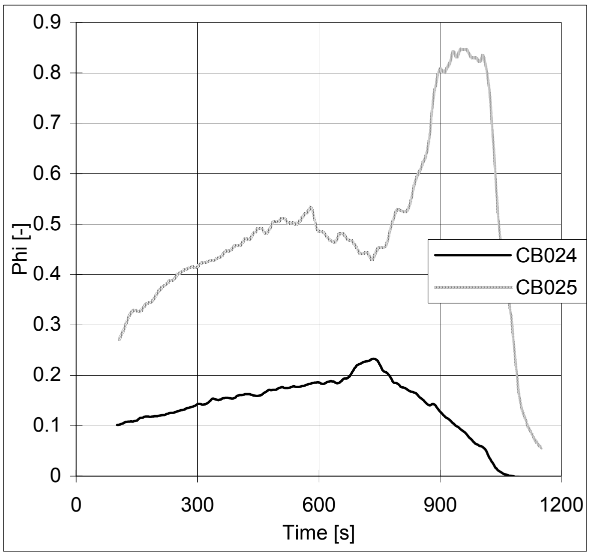
The NOx production
was not measured
during these tests.

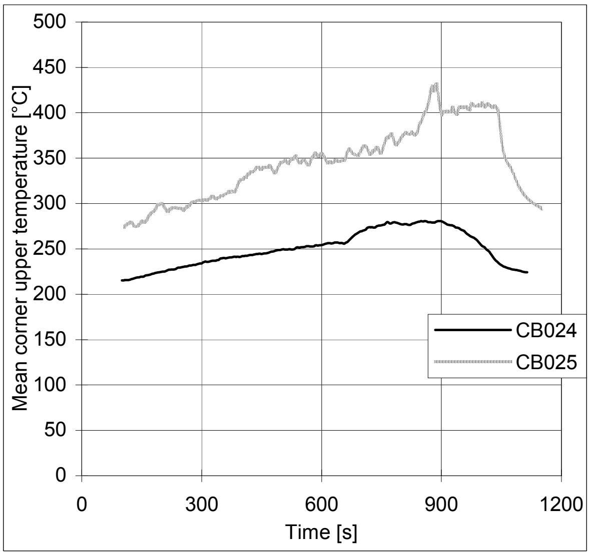
Appendix:Chlorobenzene

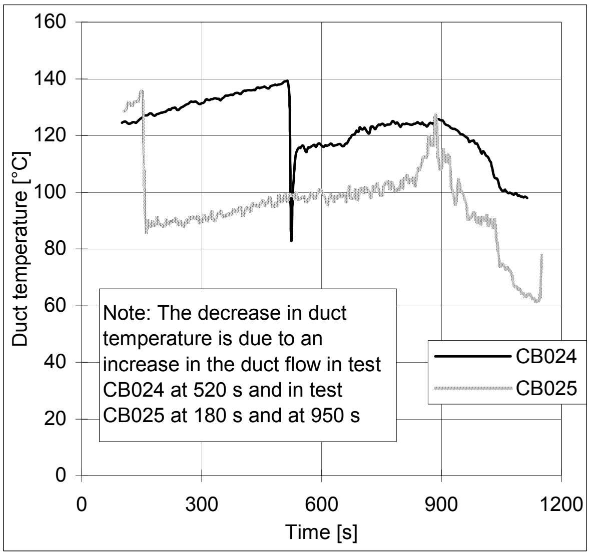




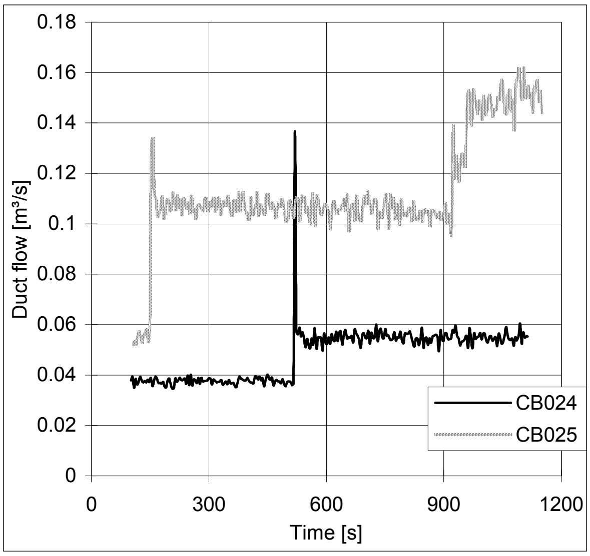


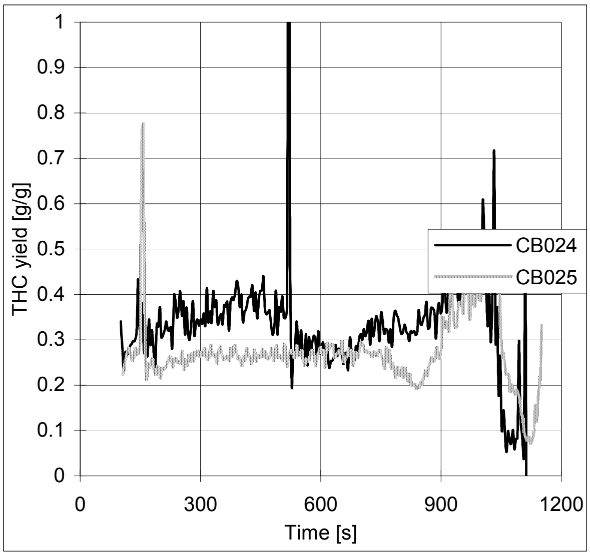


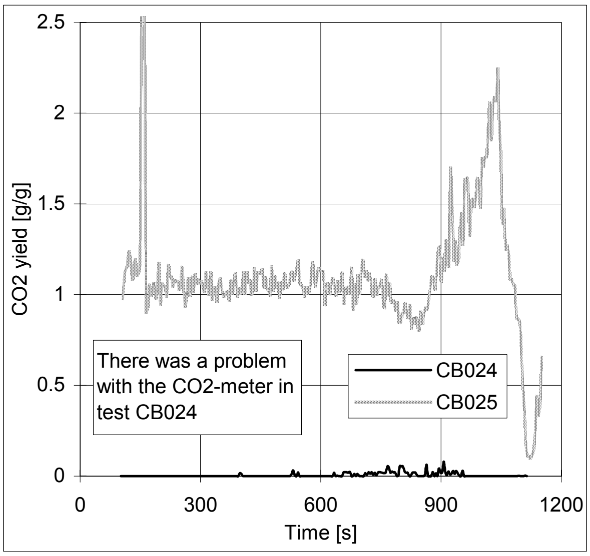




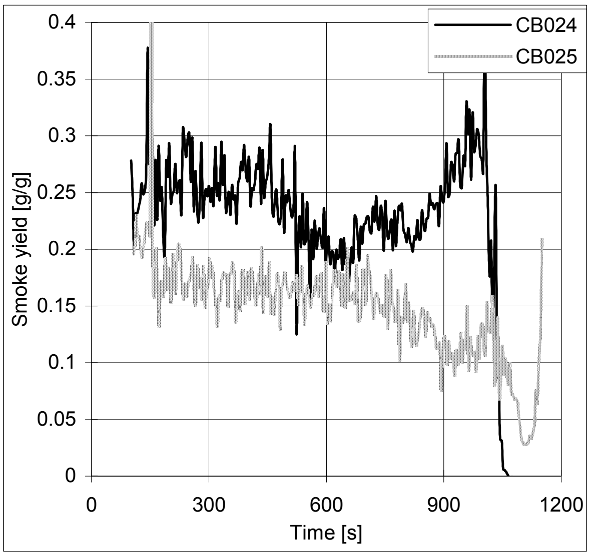
Note: The decrease in duct temperature is due to an increase in the duct flow in test CB024 at 520 s and in test CB025 at 180 s and at 950 s

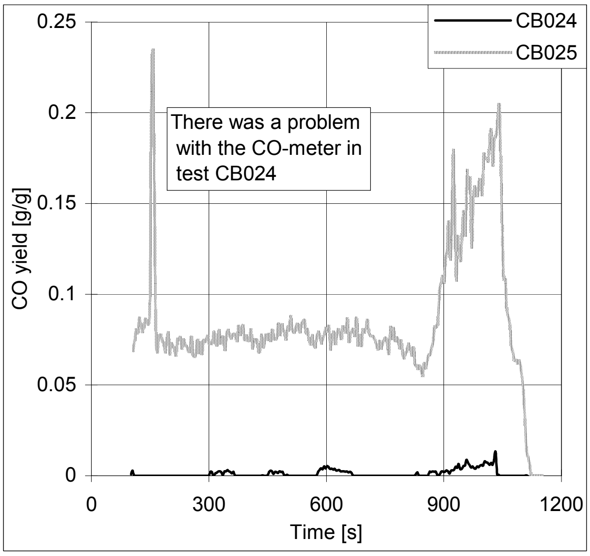






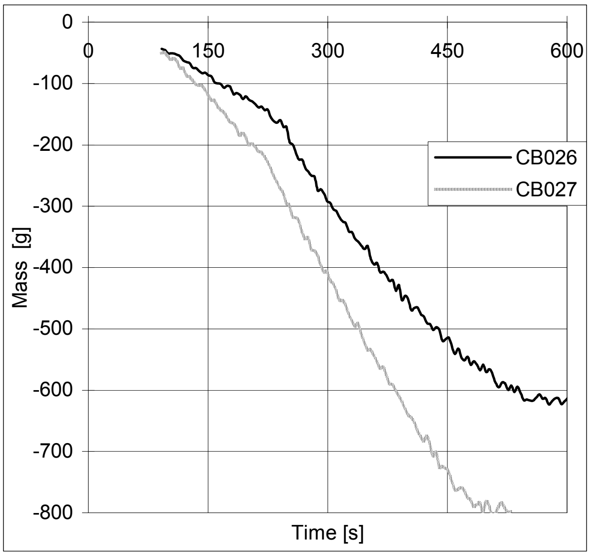
There was a problem with the CO2-meter in test CB024

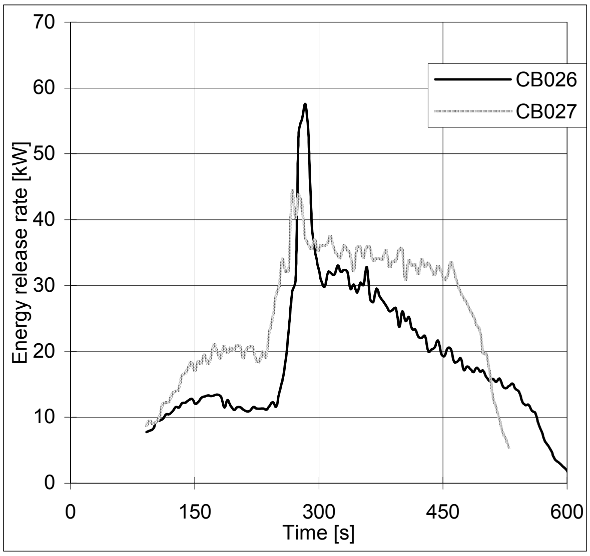


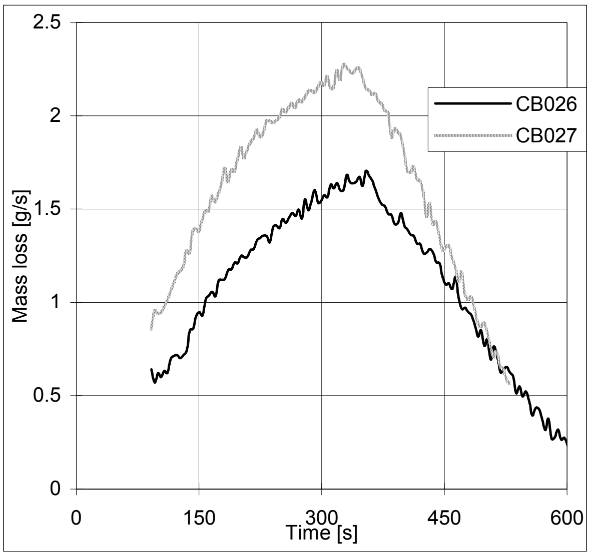


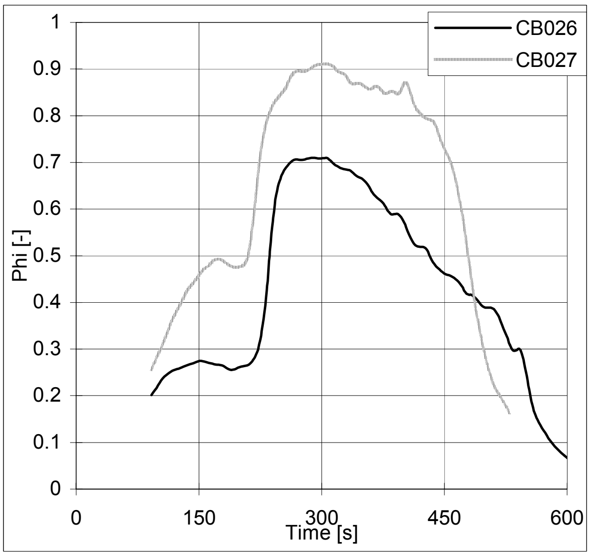
There was a problem with the CO-meter in test CB024

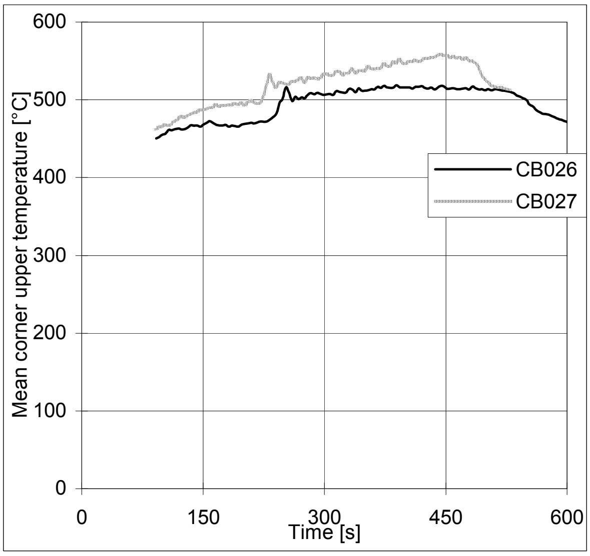
The NOx production was not measured during these tests.

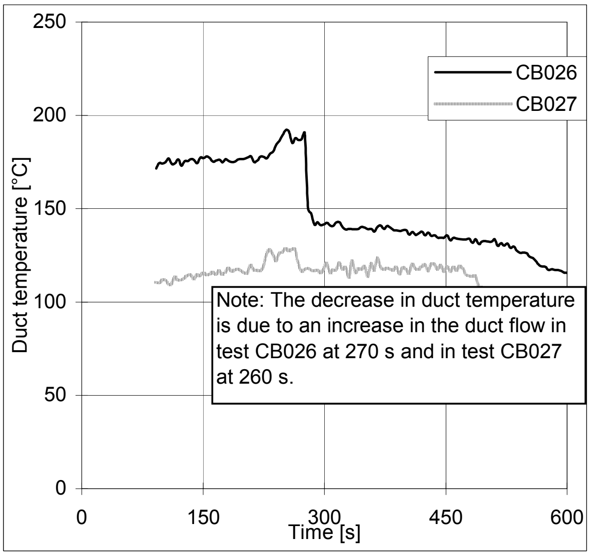




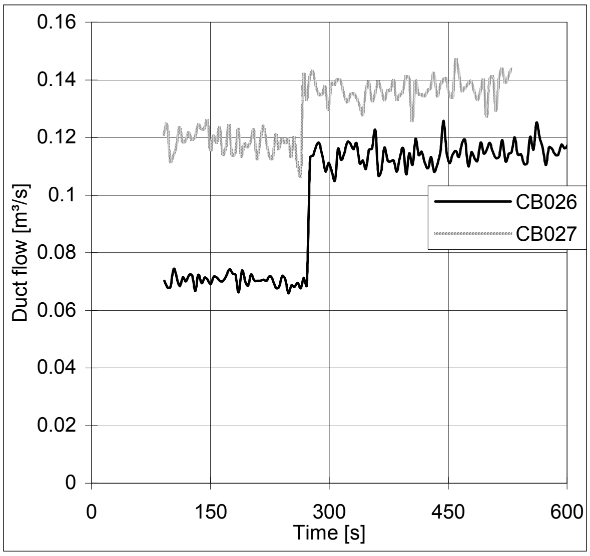


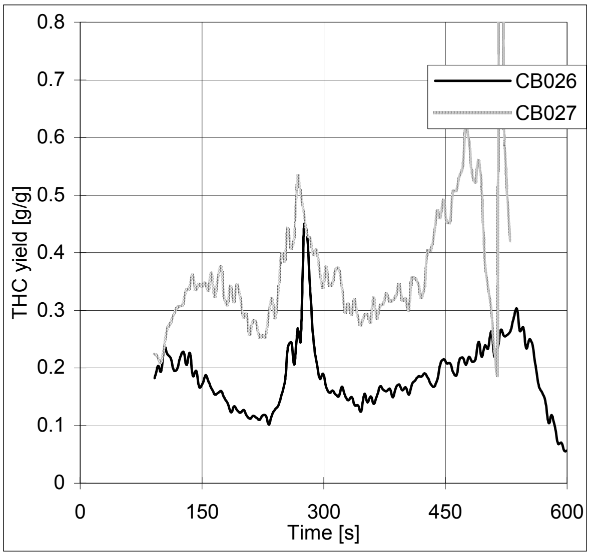


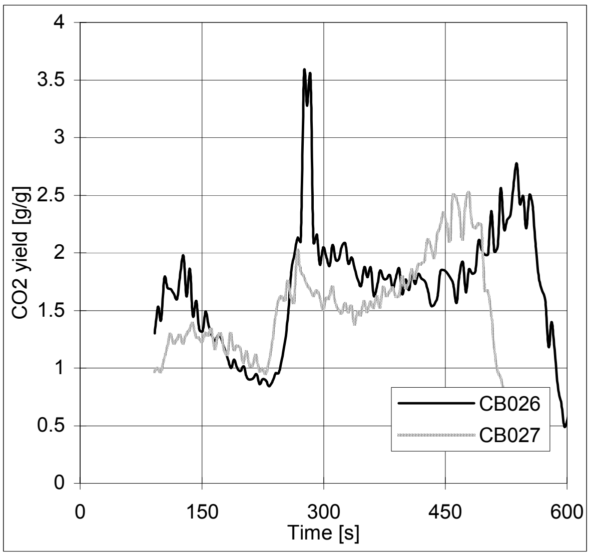


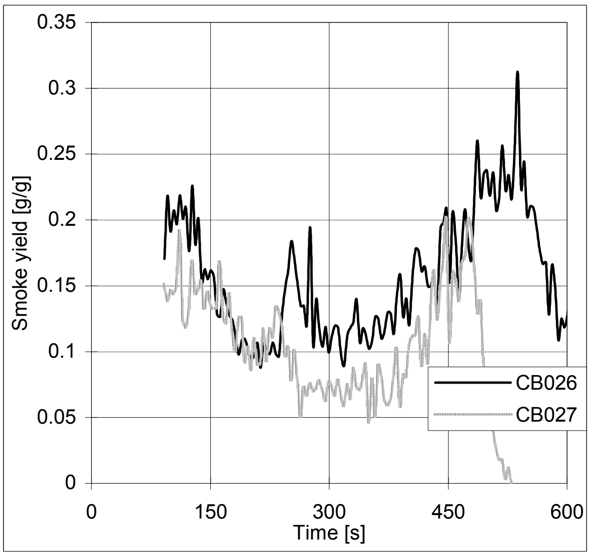


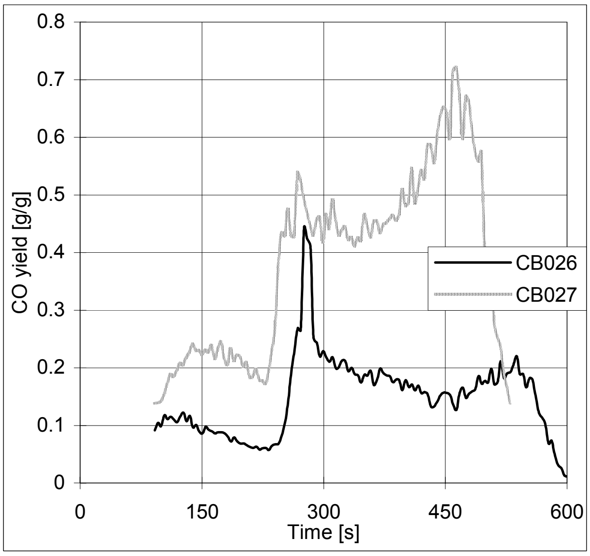
Note: The decrease in duct temperature is due to an increase in the duct flow in test CB026 at 270 s and in test CB027 at 260 s.





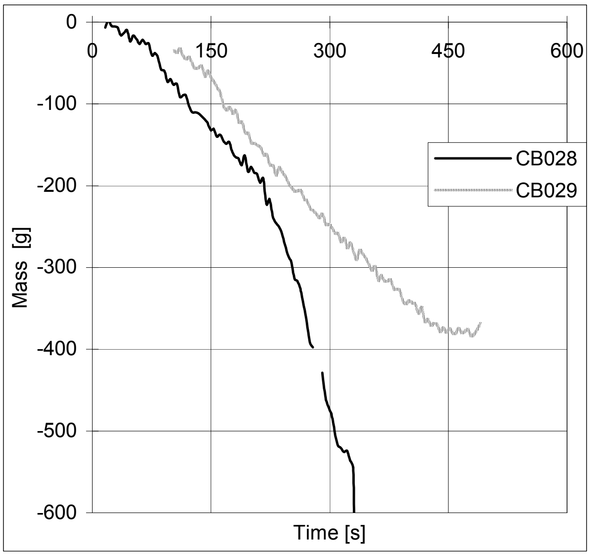


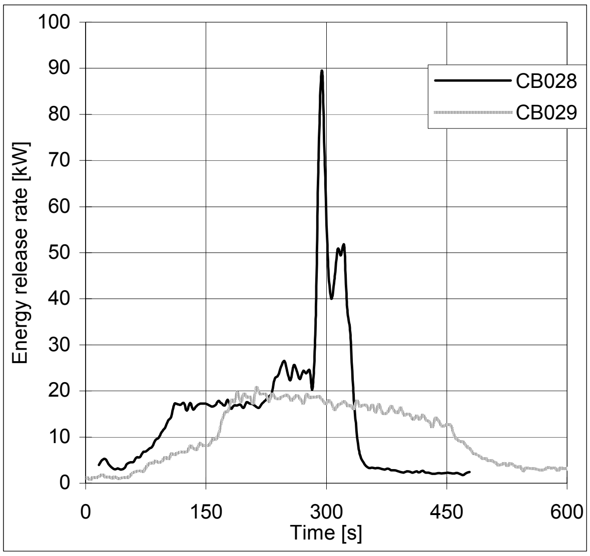


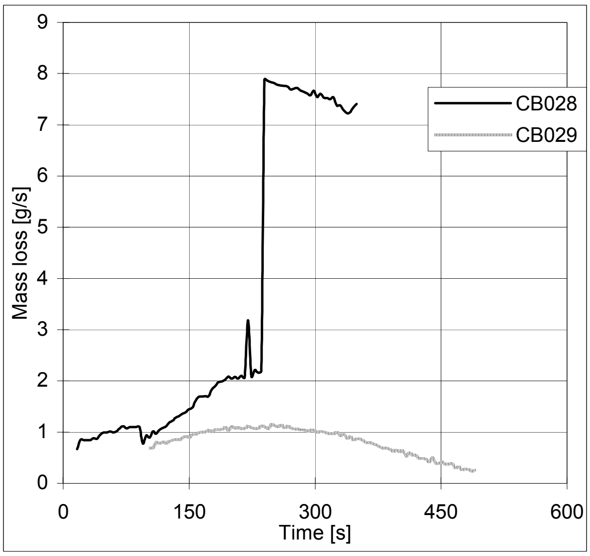


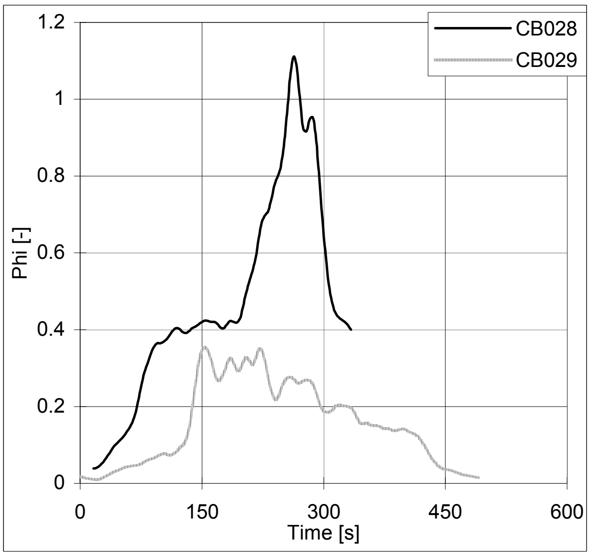
The NOx production
was not measured
during this test.

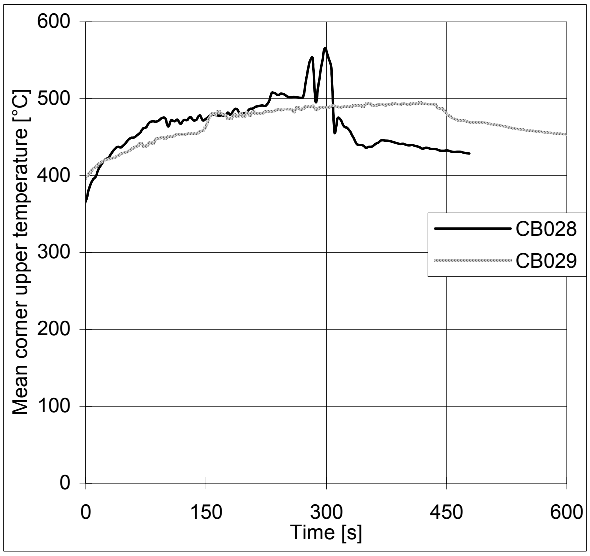
Appendix:Chlorobenzene

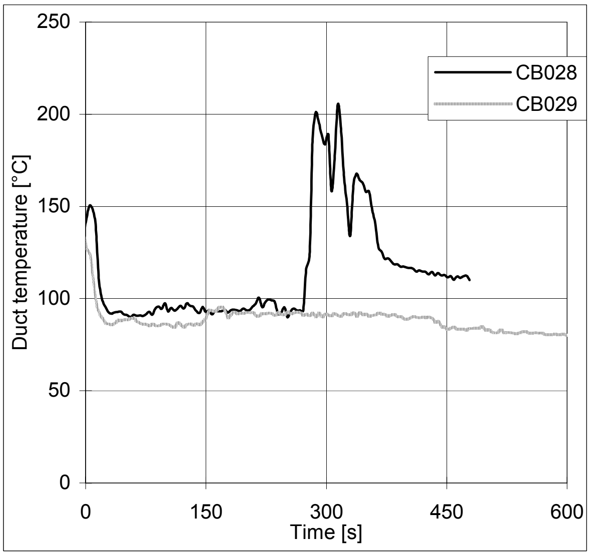




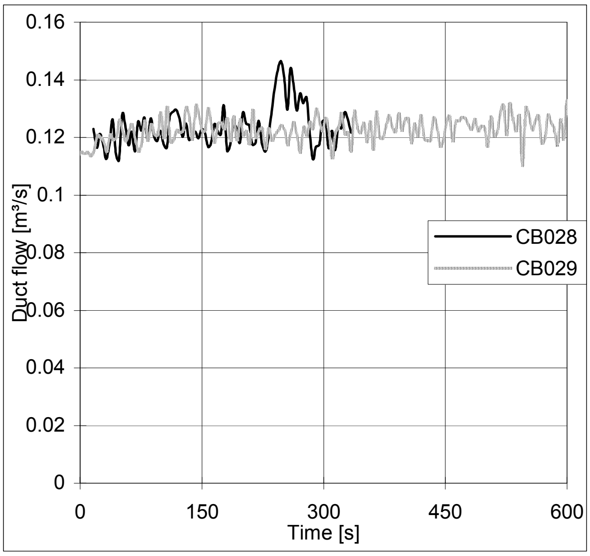


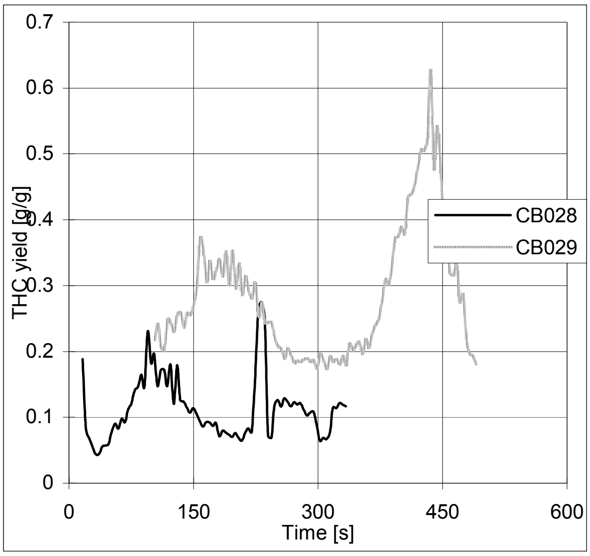


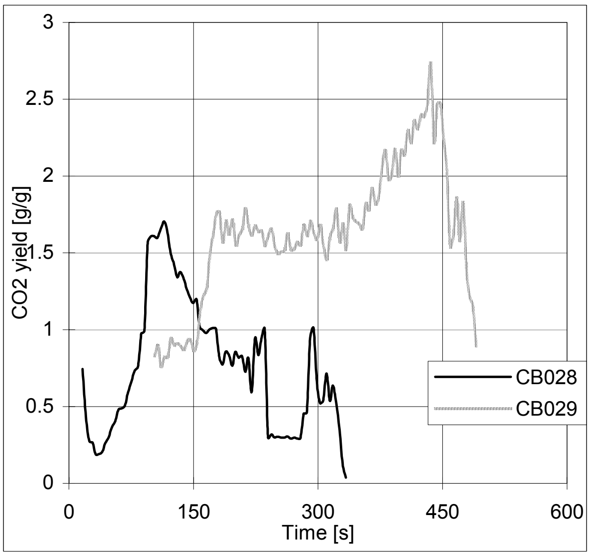


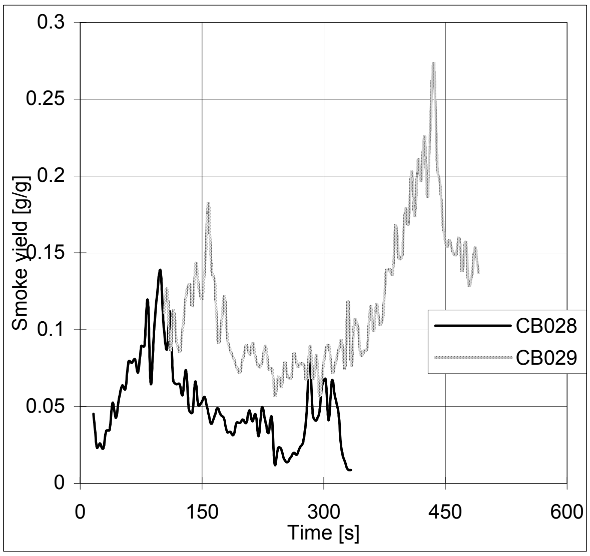


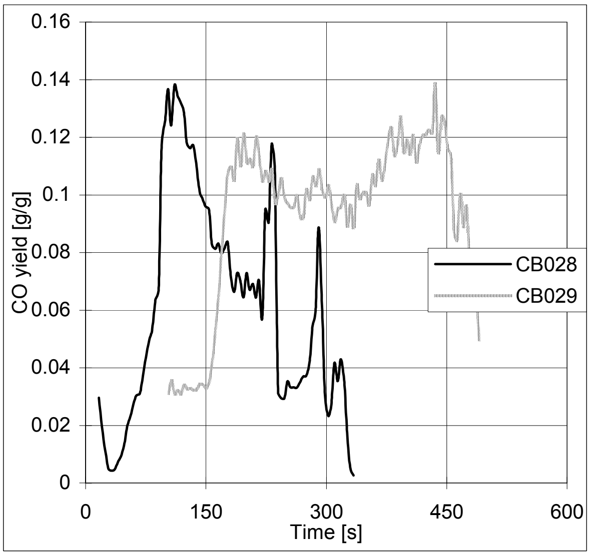
Appendix:Chlorobenzene





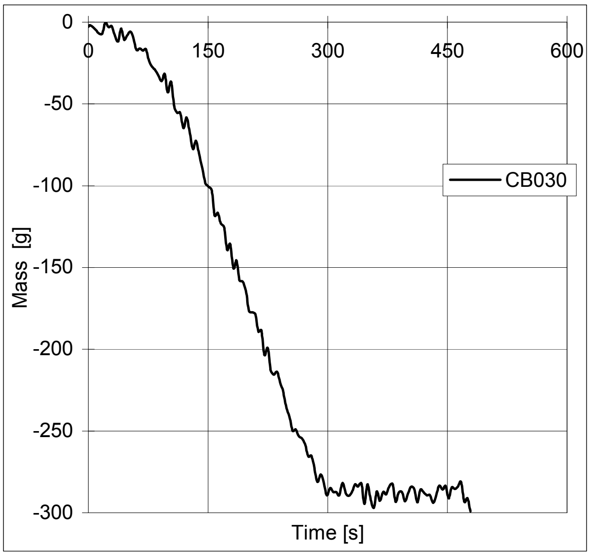


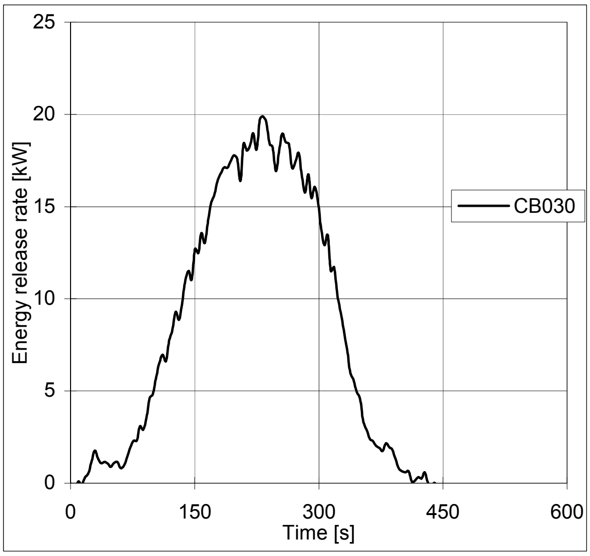


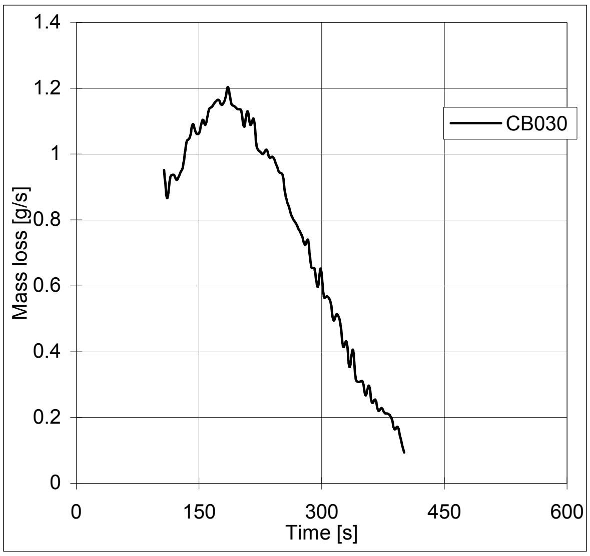


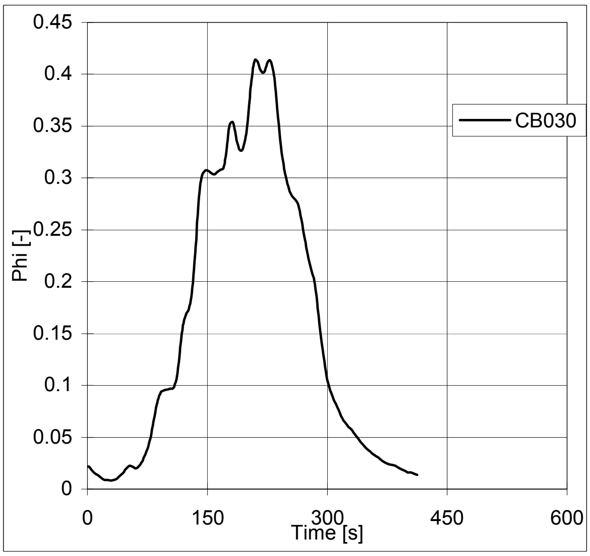
The NOx production
was not measured
during these tests.

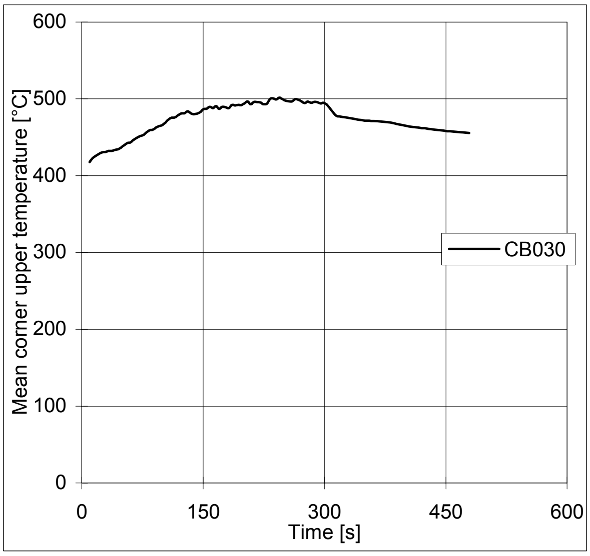
Appendix:Chlorobenzene

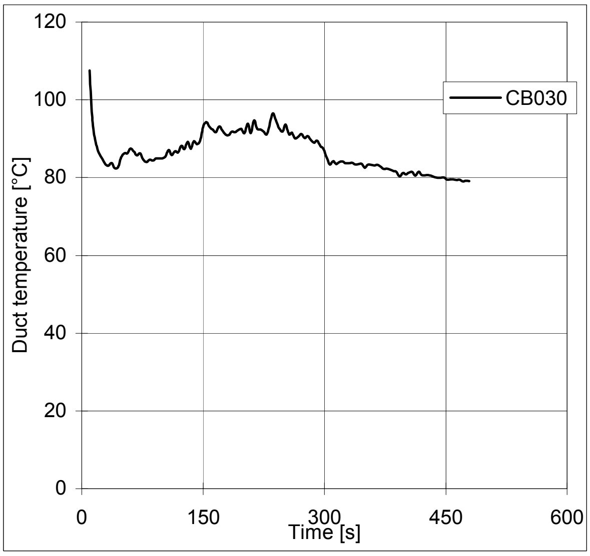


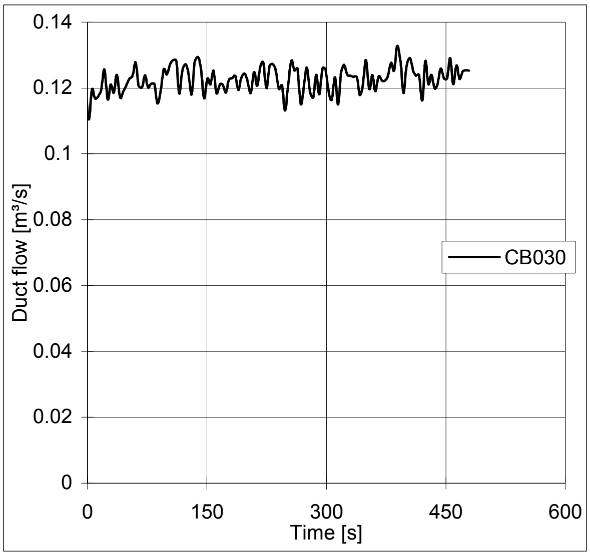


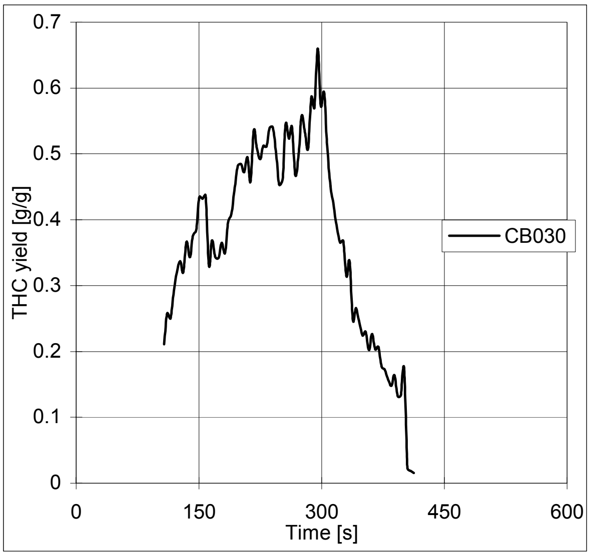


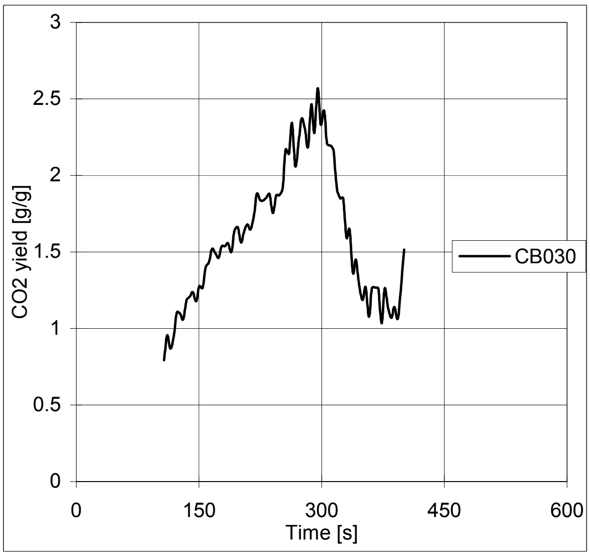


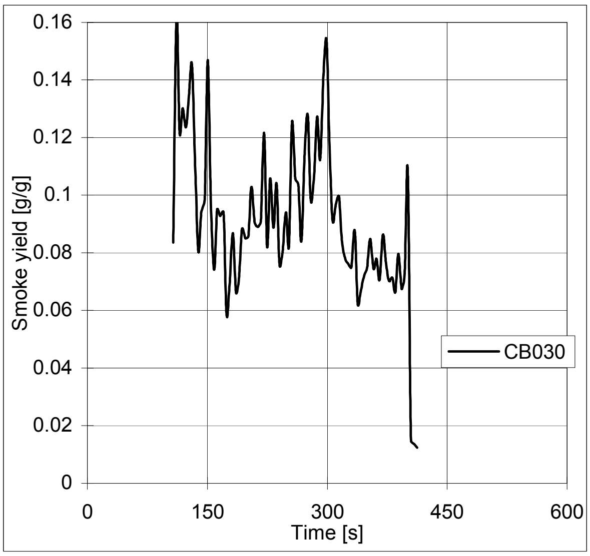


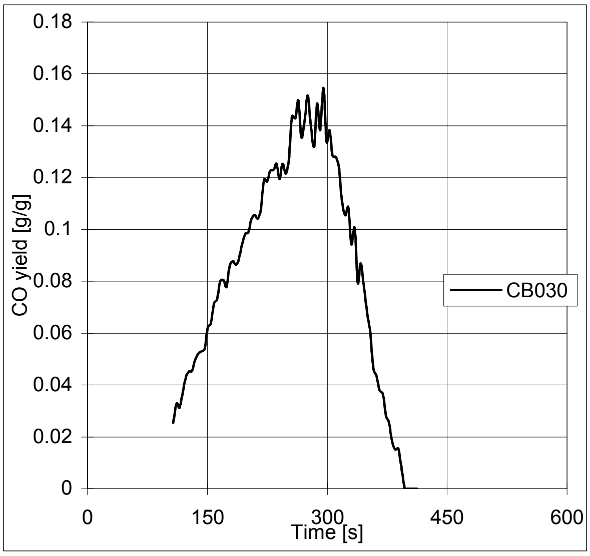


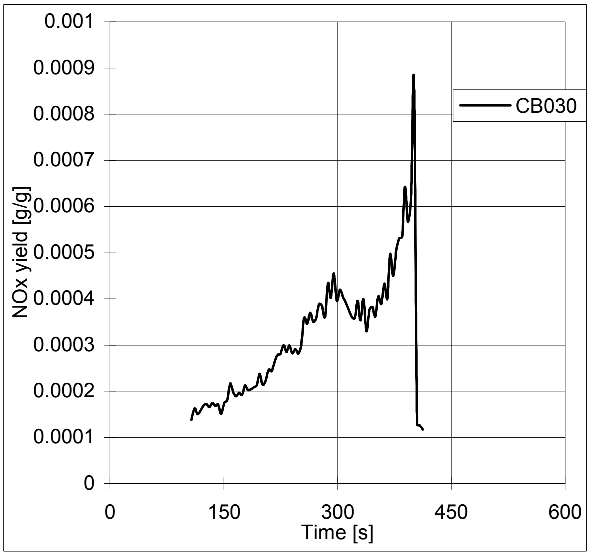

Duct flow [m³/s]
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0
150
300
450
600
Time [s]
CB030

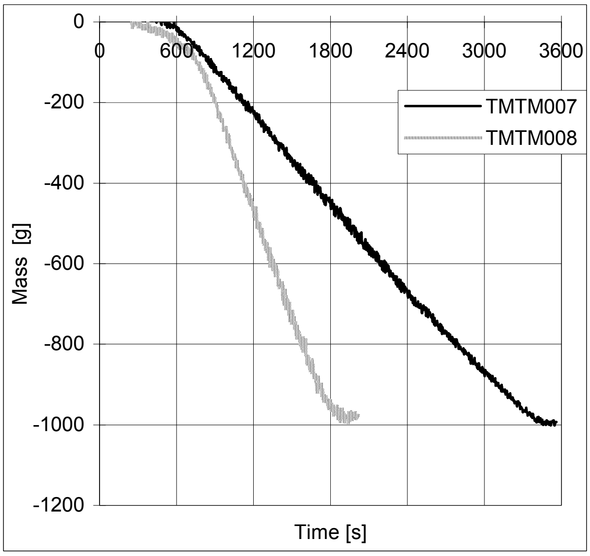

THC yield [g/g]
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
150
300
450
600
Time [s]
CB030

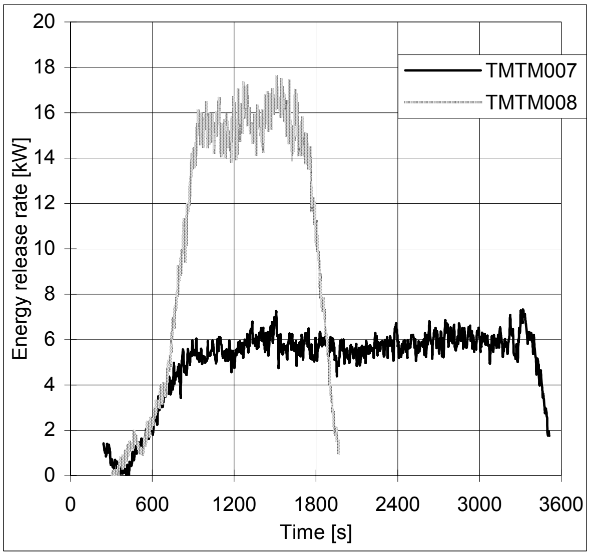

CO2 yield [g/g]
0
0.5
1
1.5
2
2.5
3
0
150
300
450
600
Time [s]
CB030

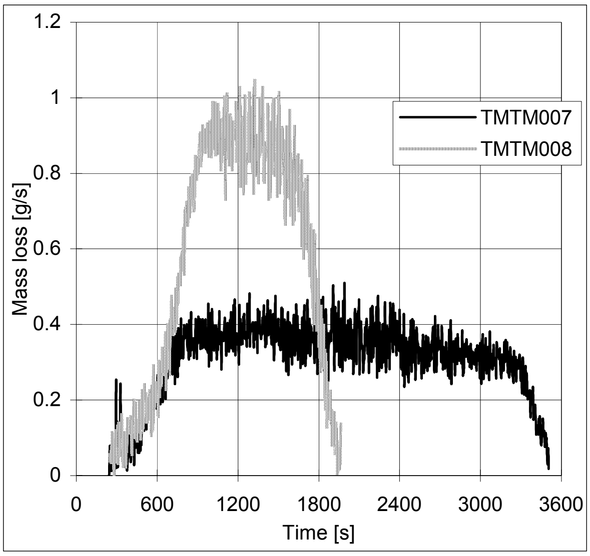

Smoke yield [g/g]
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0
150
300
450
600
Time [s]
CB030

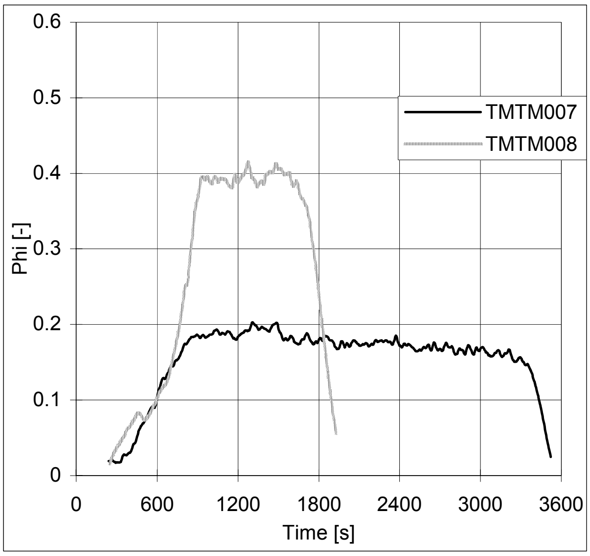

CO yield [g/g]
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0
150
300
450
600
Time [s]
CB030

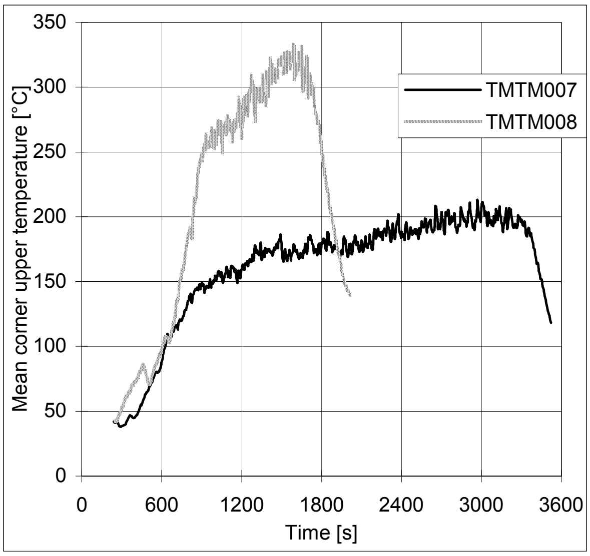

NOx yield [g/g]
0
0.0001
0.0002
0.0003
0.0004
0.0005
0.0006
0.0007
0.0008
0.0009
0.001
0
150
300
450
600
Time [s]
CB030

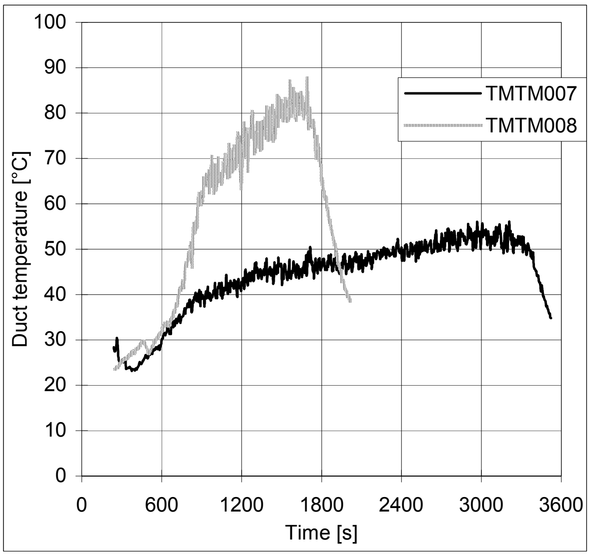

Mass [g]
0
-200
-400
-600
-800
-1000
-1200
0
600
1200
1800
2400
3000
3600
Time [s]
TMTM007
TMTM008

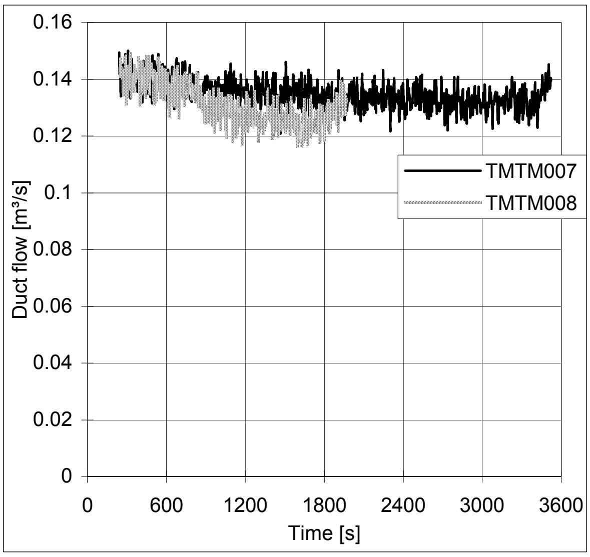

Energy release rate [kW]
20
18
16
14
12
10
8
6
4
2
0
0
600
1200
1800
2400
3000
3600
Time [s]
TMTM007
TMTM008


Mass loss [g/s]
1.2
1
0.8
0.6
0.4
0.2
0
0
600
1200
1800
2400
3000
3600
Time [s]
TMTM007
TMTM008

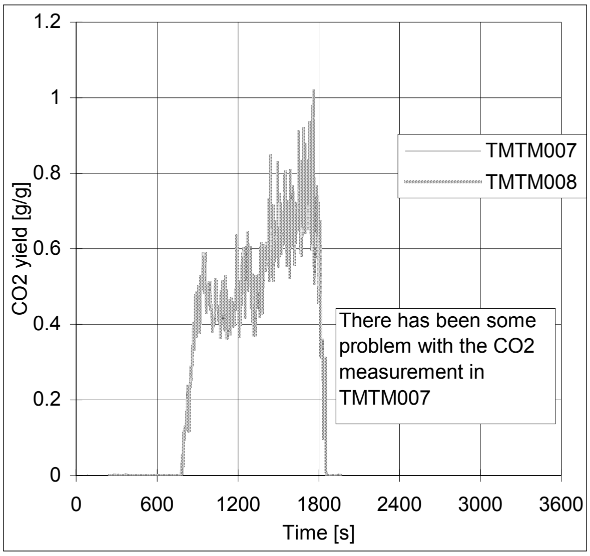

Phi [-]
0.6
0.5
0.4
0.3
0.2
0.1
0
0
600
1200
1800
2400
3000
3600
Time [s]
TMTM007
TMTM008


Mean corner upper temperature [°C]
350
300
250
200
150
100
50
0
0
600
1200
1800
2400
3000
3600
Time [s]
TMTM007
TMTM008


Duct temperature [°C]
100
90
80
70
60
50
40
30
20
10
0
0
600
1200
1800
2400
3000
3600
Time [s]
TMTM007
TMTM008

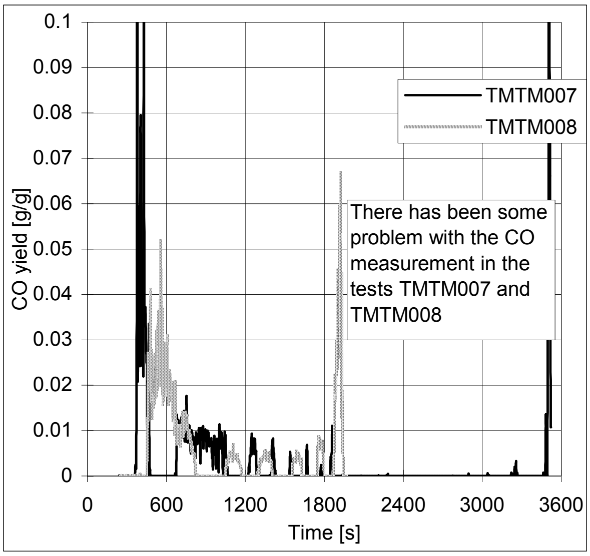


The production of THC was very low and because of this the yield of THC was not calculated.

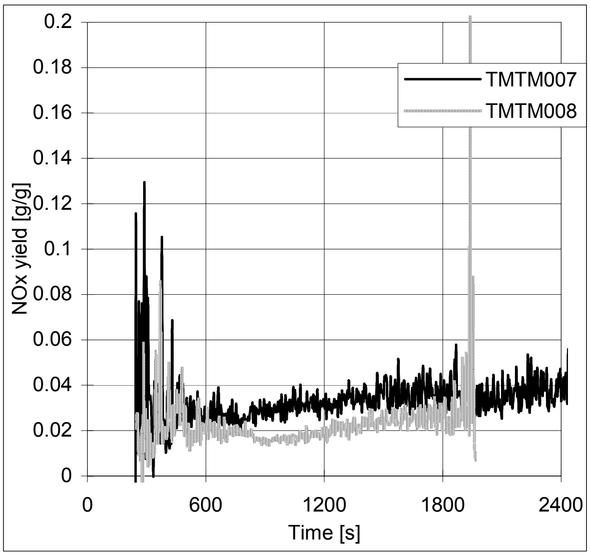


There has been some problem with the CO2 measurement in TMTM007

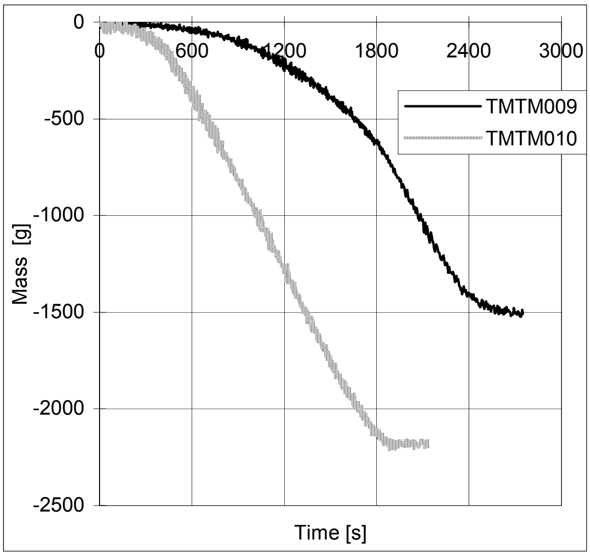
The smoke production was very low and because of this the yield of smoke was not calculated.

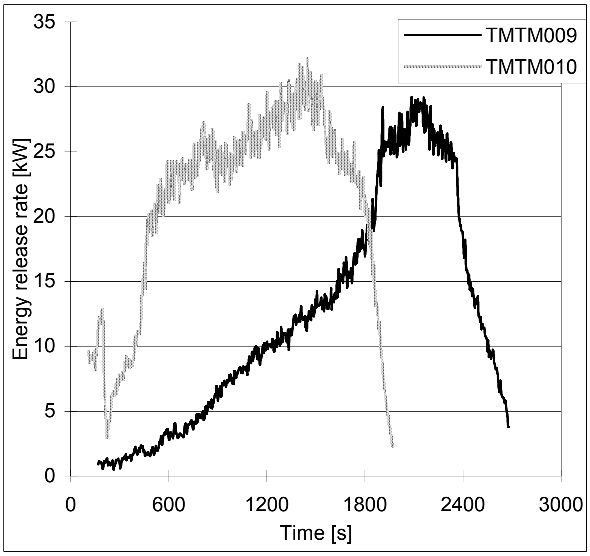


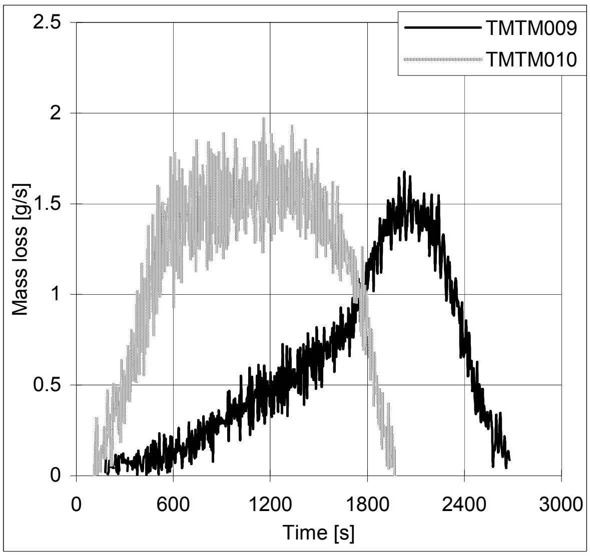
There has been some problem with the CO measurement in the tests TMTM007 and TMTM008

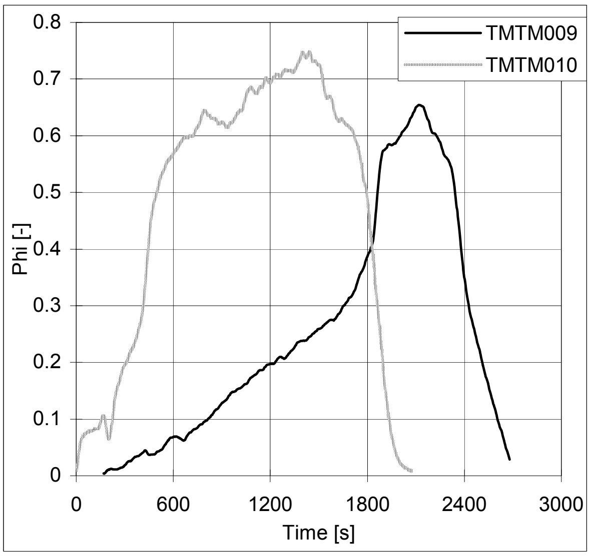


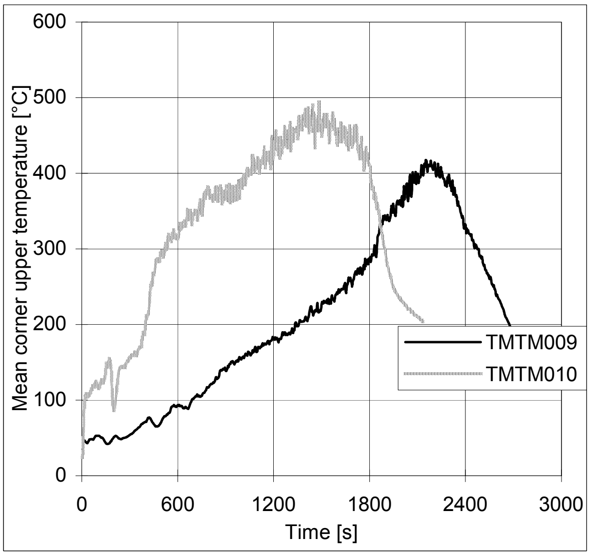
Appendix: TMTM

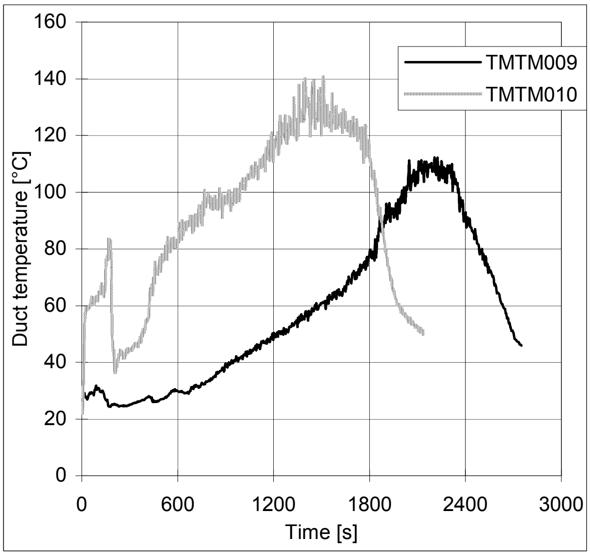




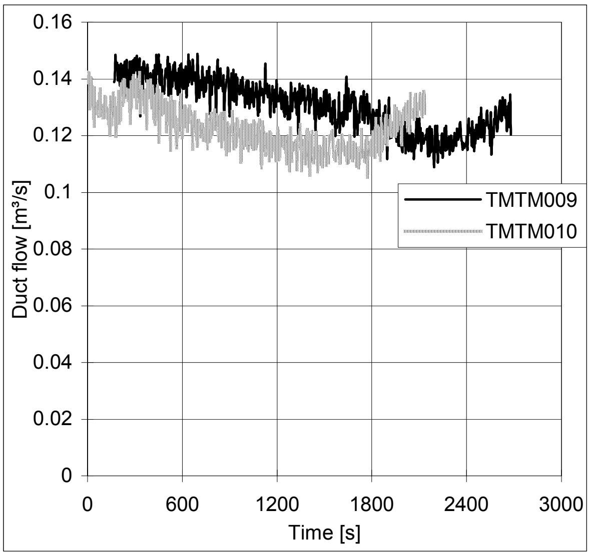




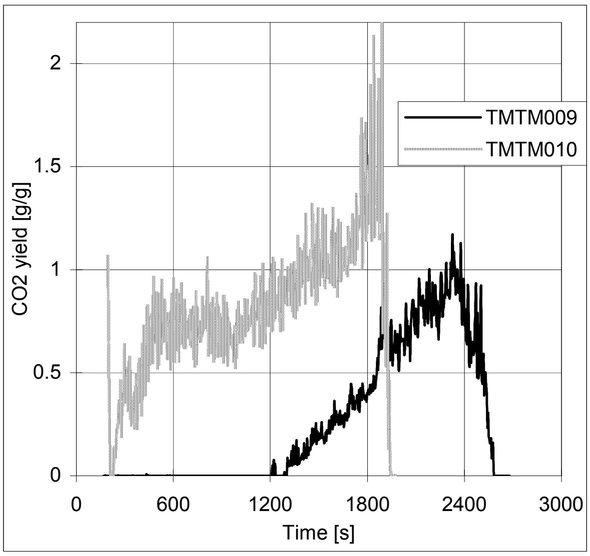




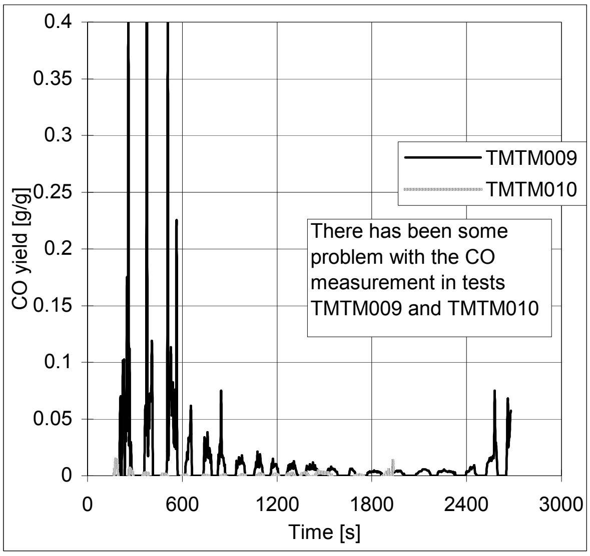
Appendix: TMTM



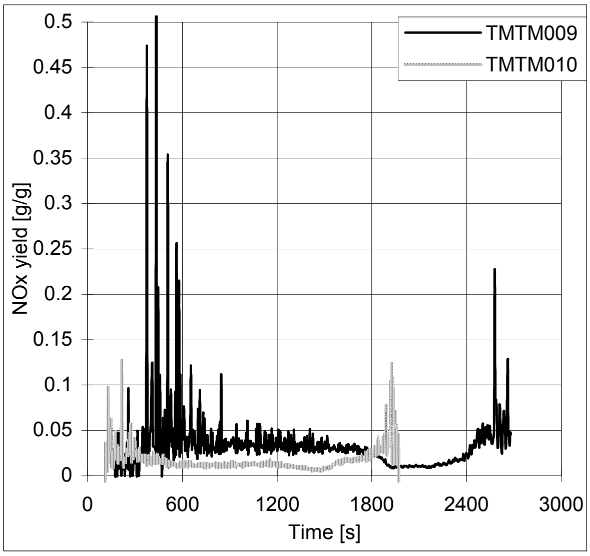
The production of THC was very low and because of this the yield of THC was not calculated.

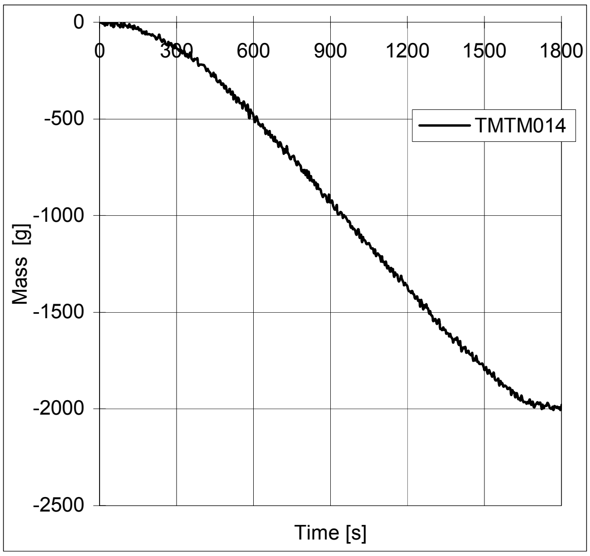


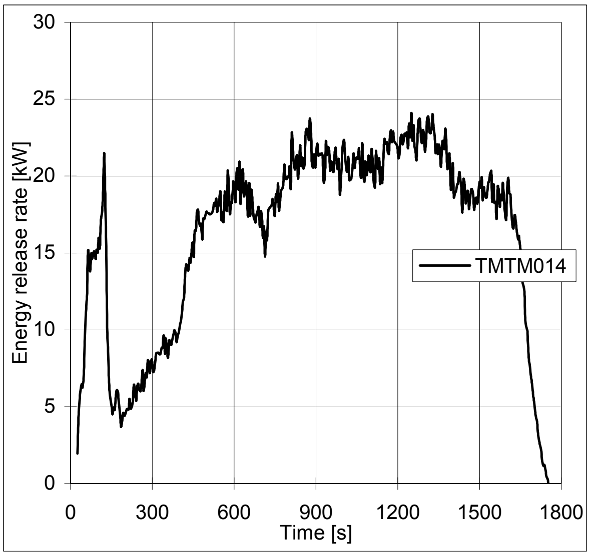
The smoke production was very low and because of this the yield of smoke was not calculated.

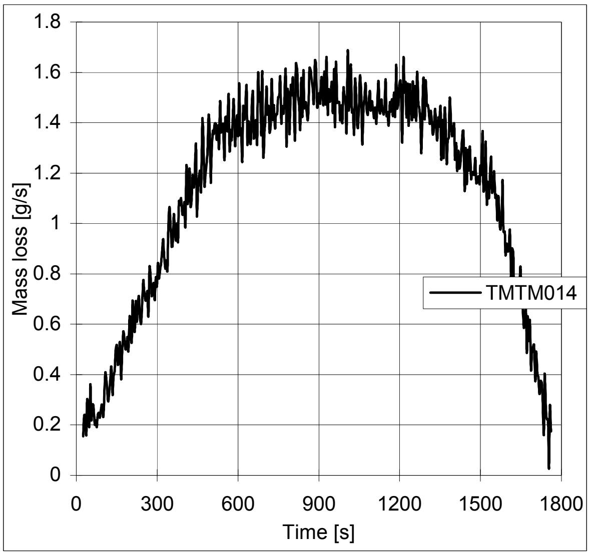


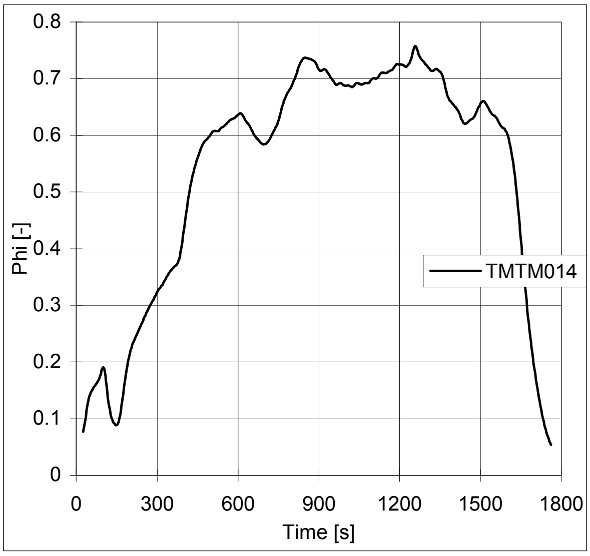
There has been some problem with the CO measurement in tests TMTM009 and TMTM010

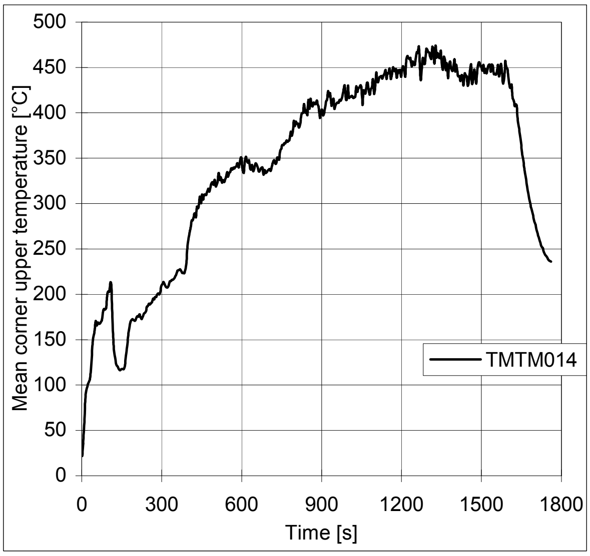


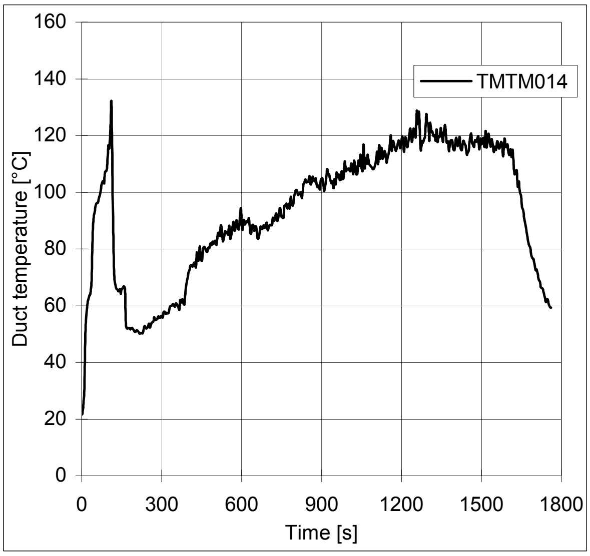

0
-500
-1000
-1500
-2000
-2500
0
300
600
900
1200
1500
1800
Mass [g]
Time [s]
TMTM014

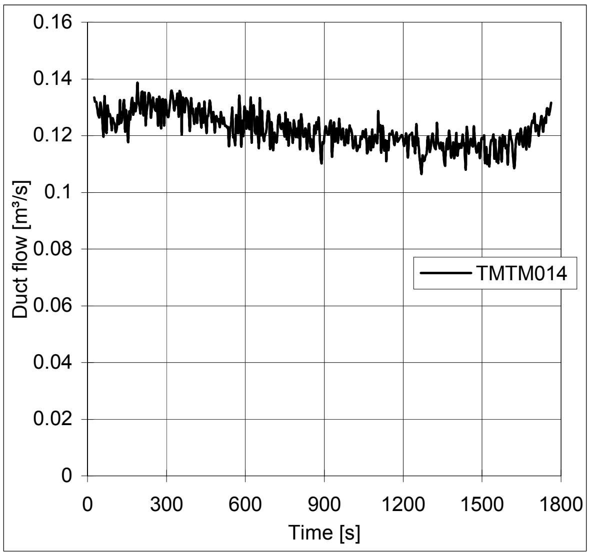

30
25
20
15
10
5
0
0
300
600
900
1200
1500
1800
Energy release rate [kW]
Time [s]
TMTM014


1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
300
600
900
1200
1500
1800
Mass loss [g/s]
Time [s]
TMTM014

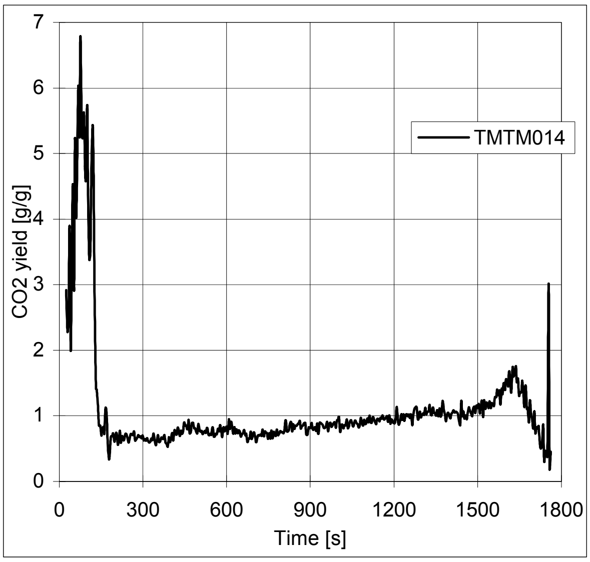

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
300
600
900
1200
1500
1800
Phi [-]
Time [s]
TMTM014


500
450
400
350
300
250
200
150
100
50
0
0
300
600
900
1200
1500
1800
Mean corner upper temperature [°C]
Time [s]
TMTM014

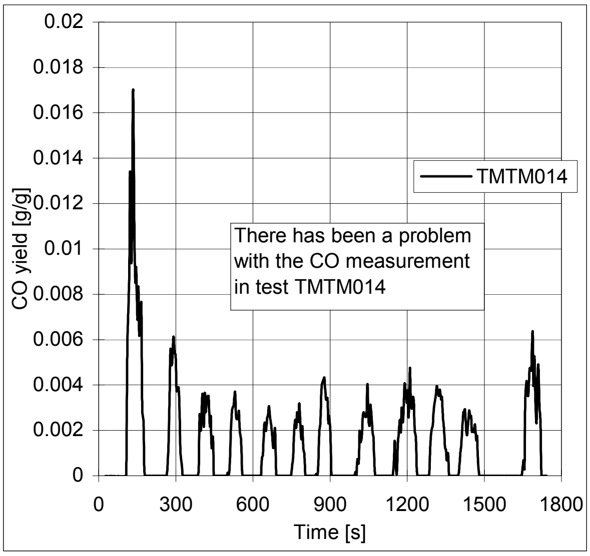

160
140
120
100
80
60
40
20
0
0
300
600
900
1200
1500
1800
Duct temperature [°C]
Time [s]
TMTM014



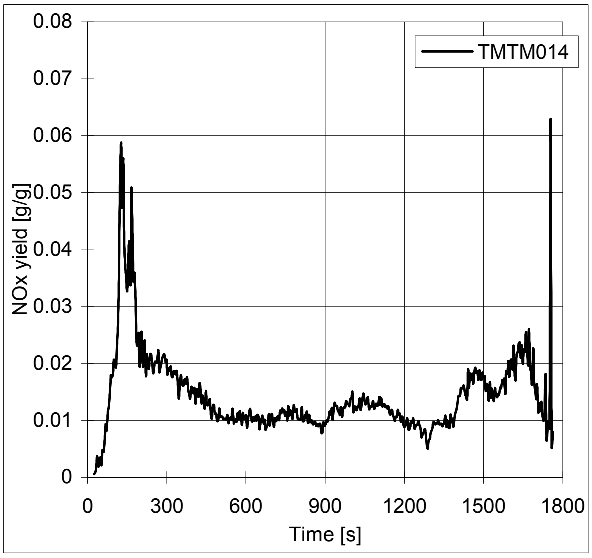
The production of THC was very low and because of this the yield of THC was not calculated.

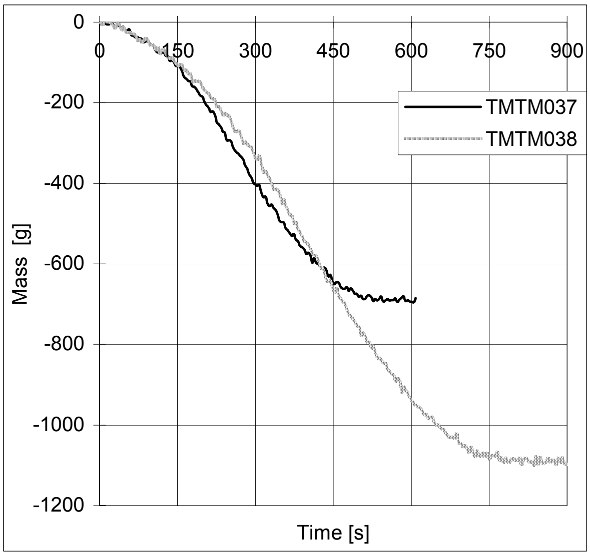


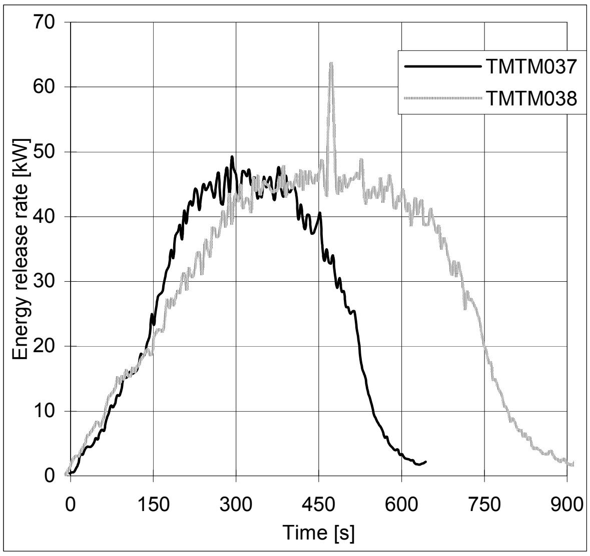
The smoke production was very low and because of this the yield of smoke was not calculated.

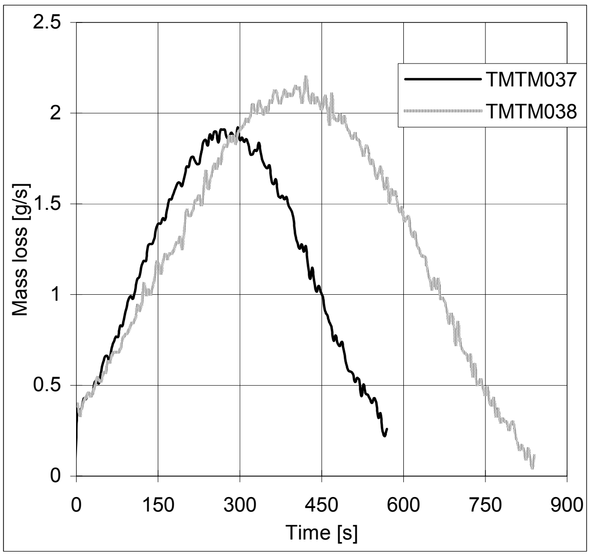


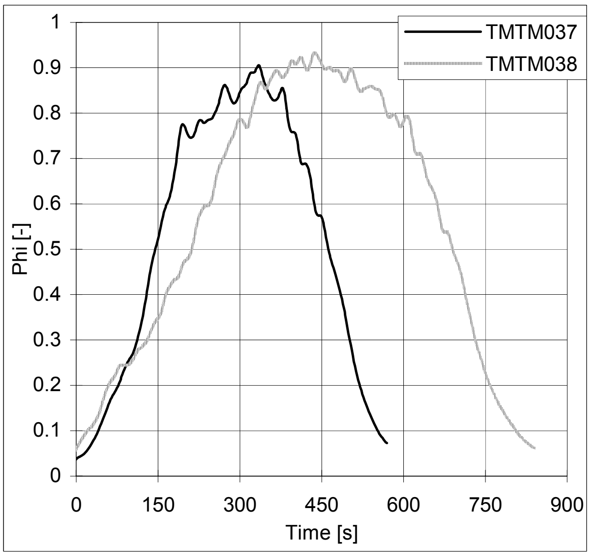
There has been a problem with the CO measurement in test TMTM014

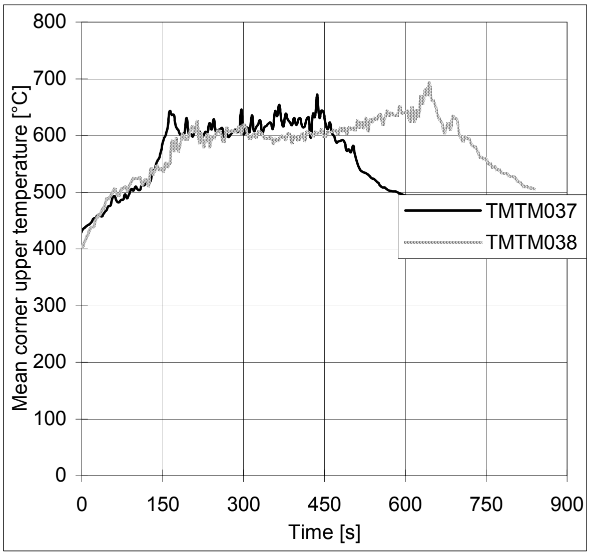


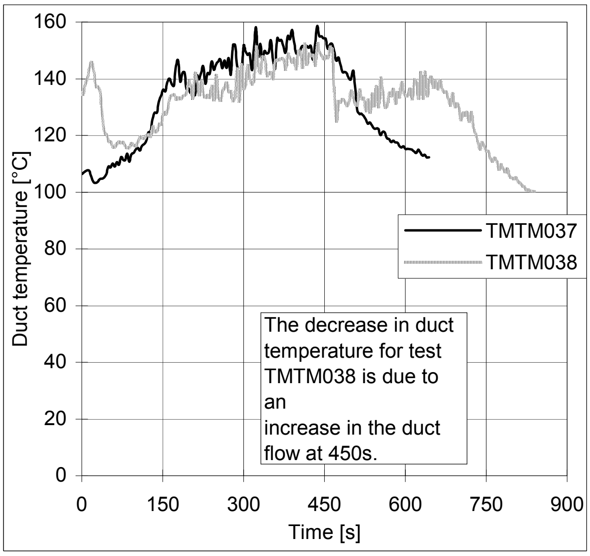




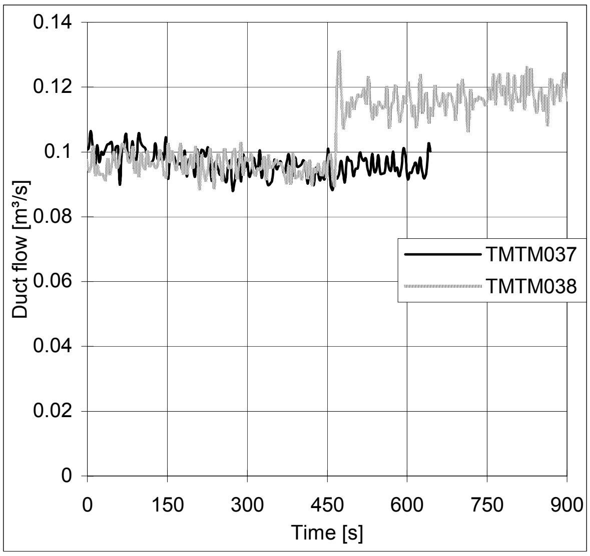


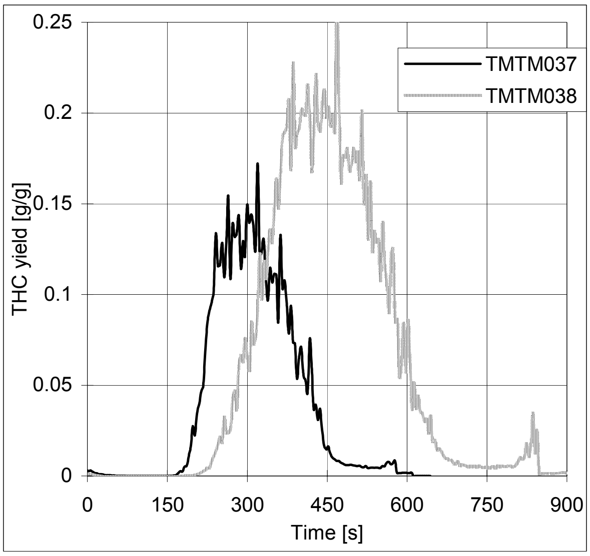


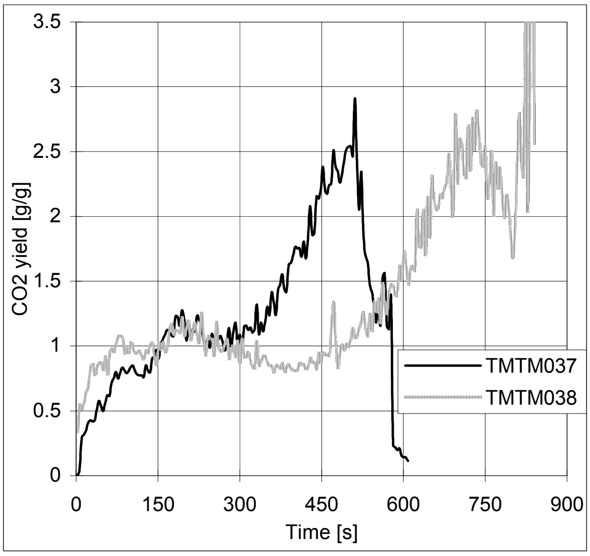




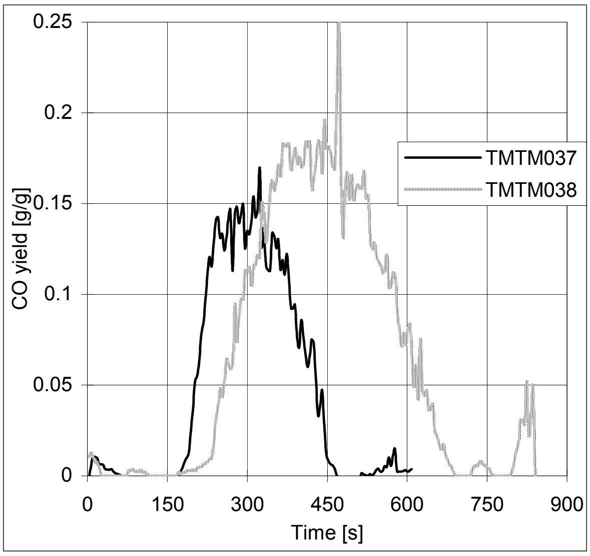
The decrease in duct temperature for test TMTM038 is due to an increase in the duct flow at 450s.

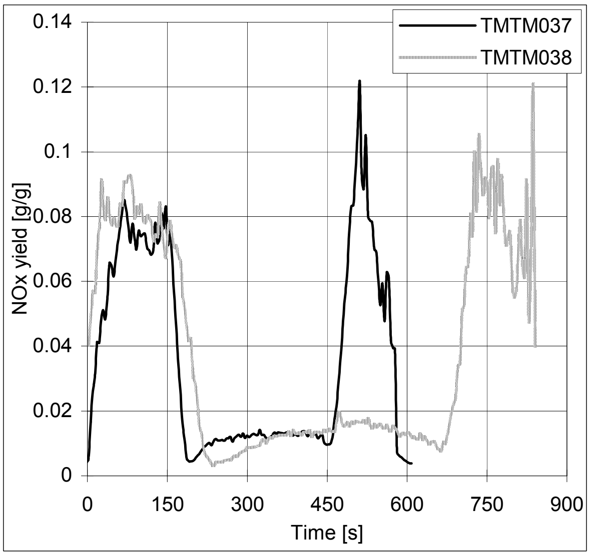




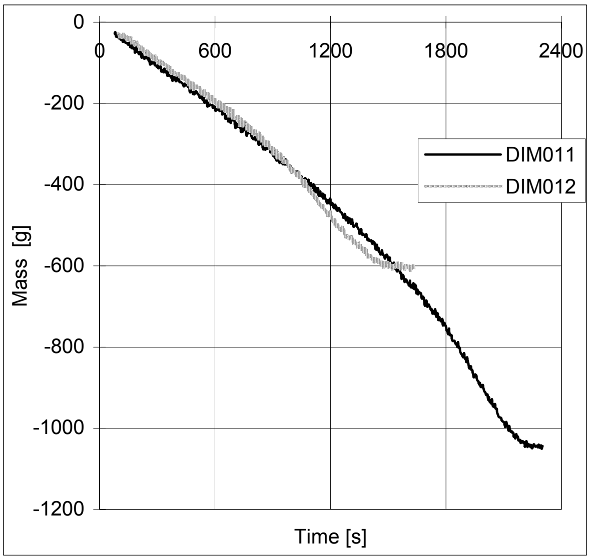


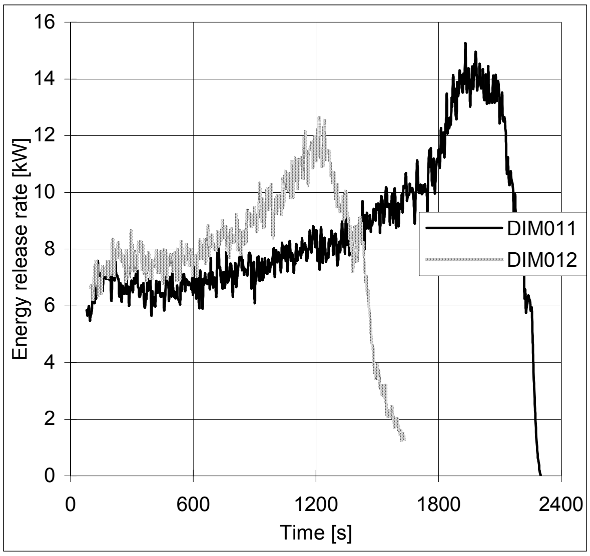
The smoke production was very low and because of this the yield of smoke was not calculated.

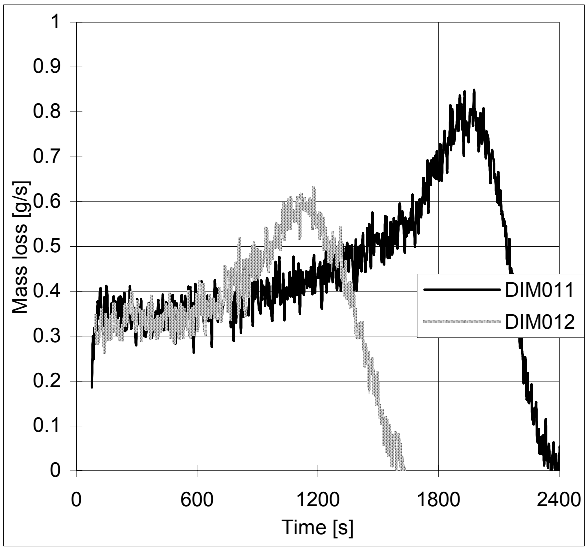


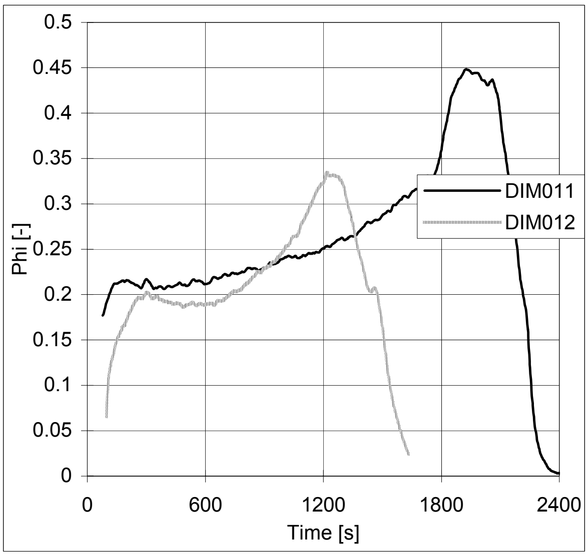


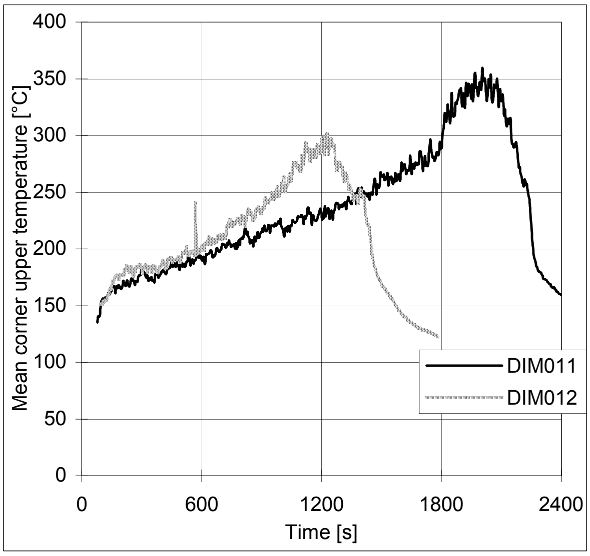
Appendix: Dimethoate

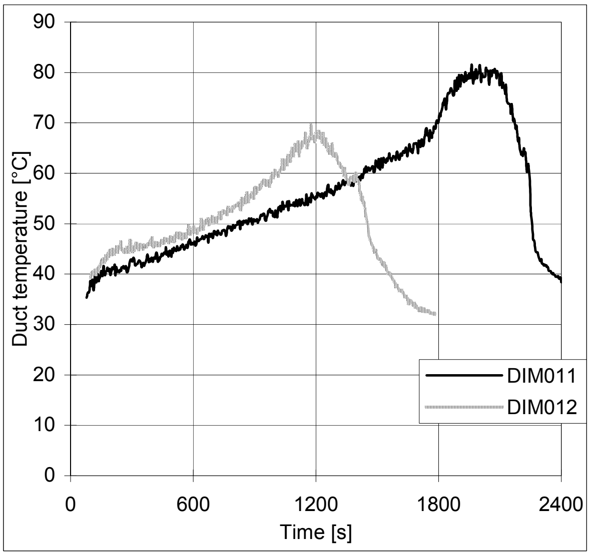




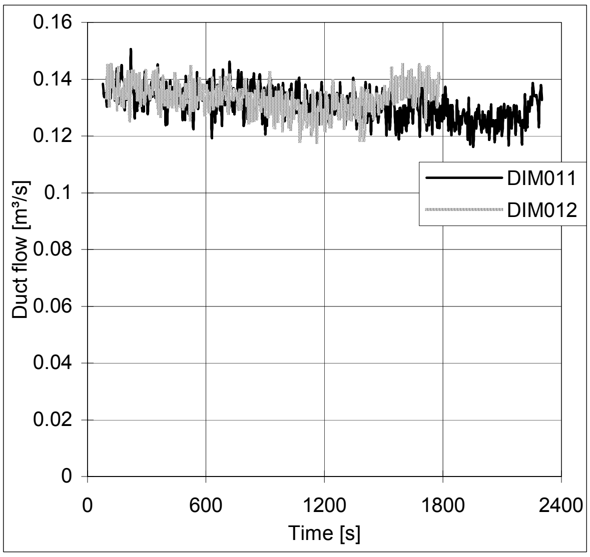


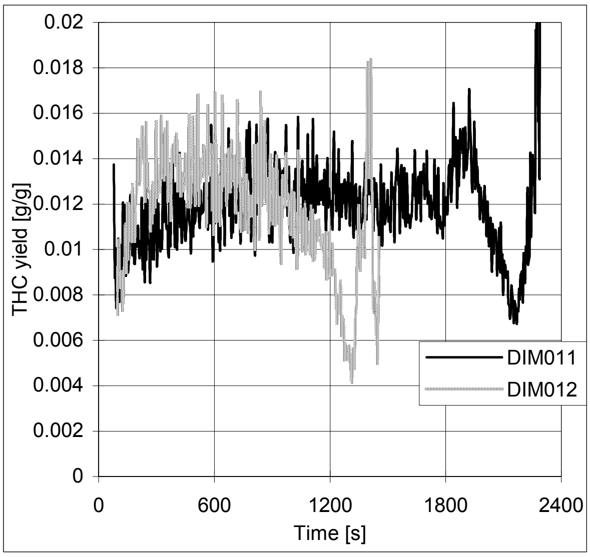


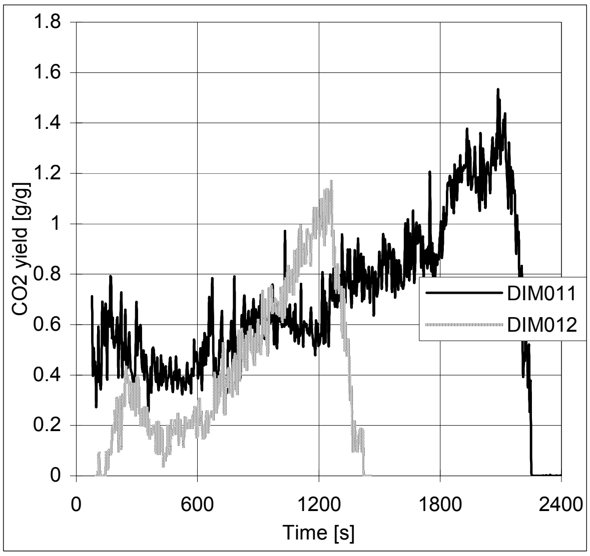


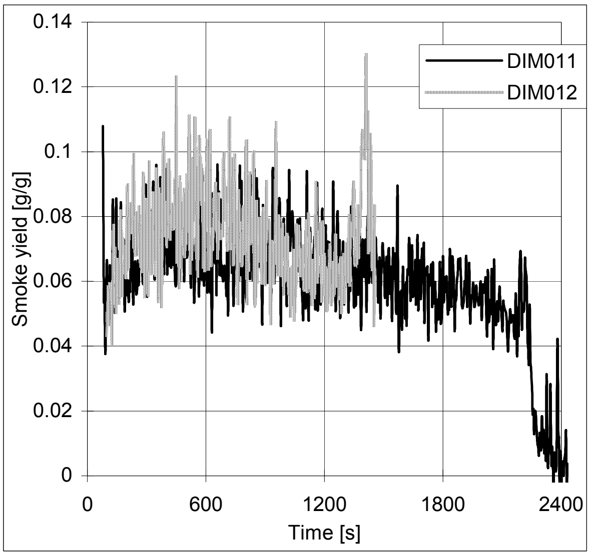


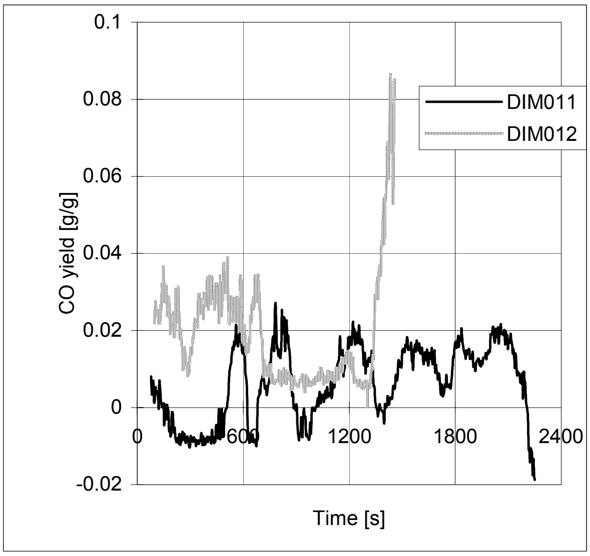
Appendix: Dimethoate

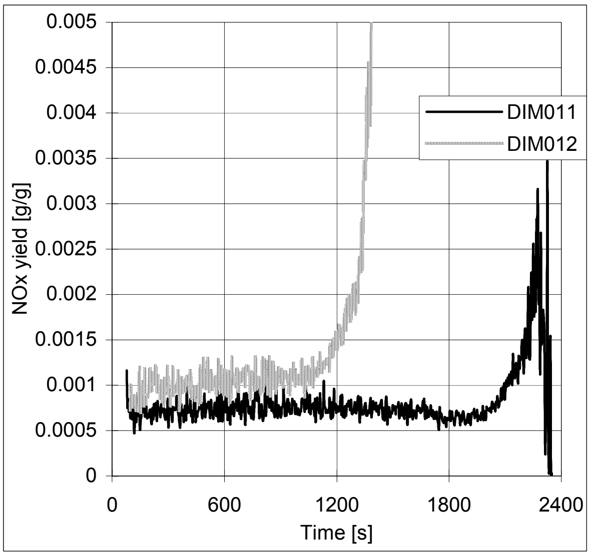




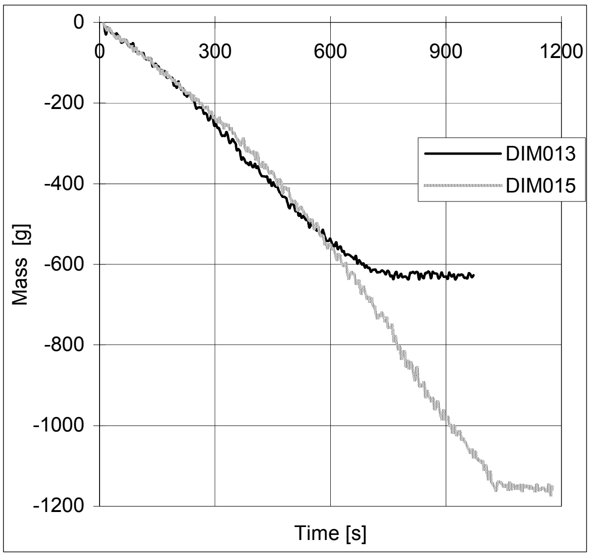


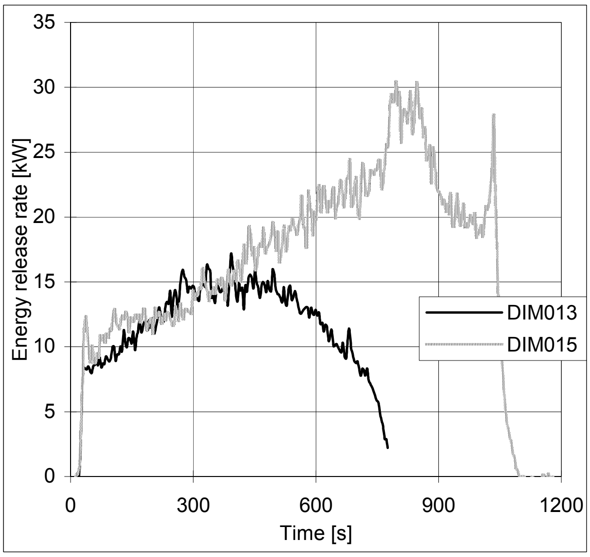


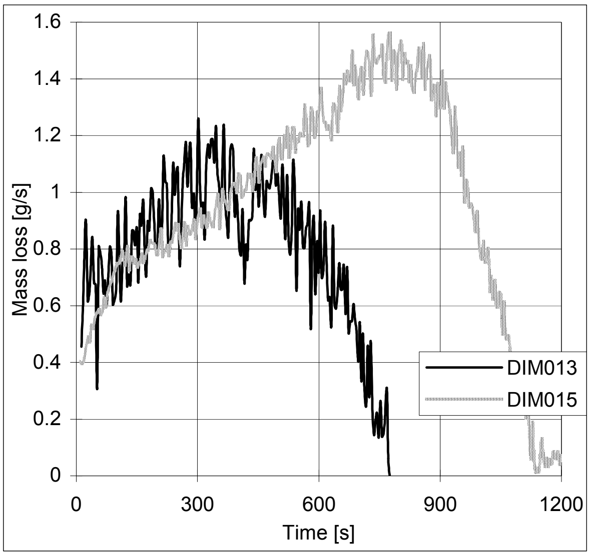


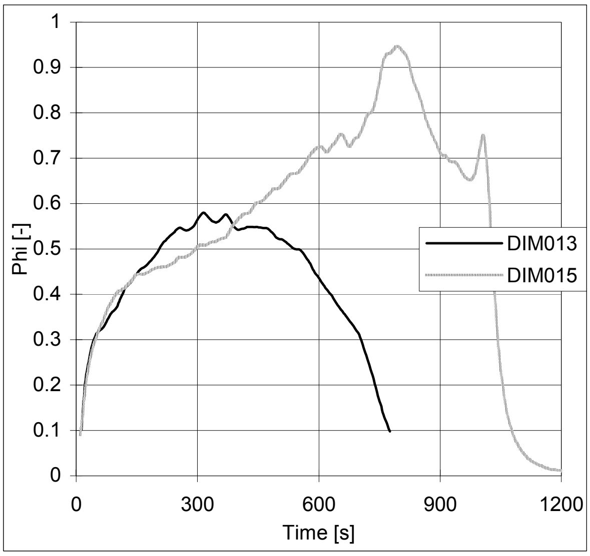


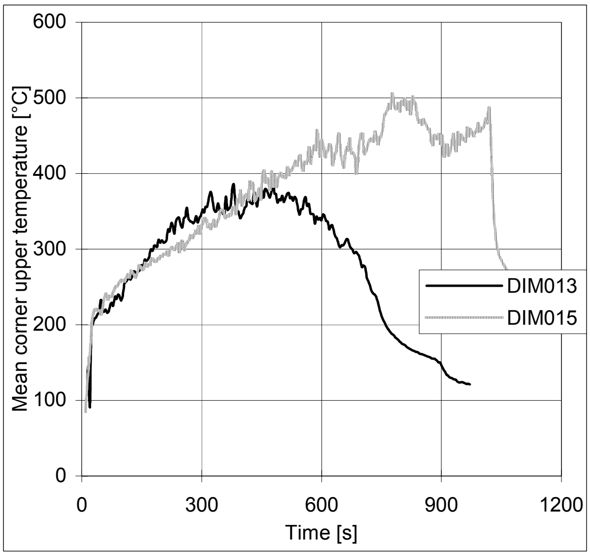
Appendix: Dimethoate

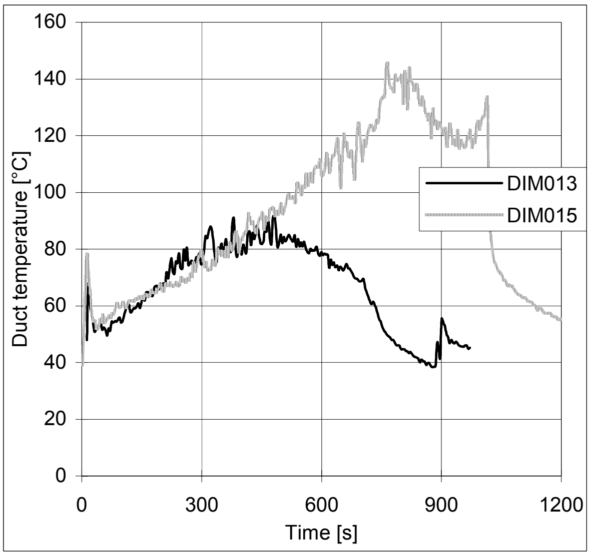


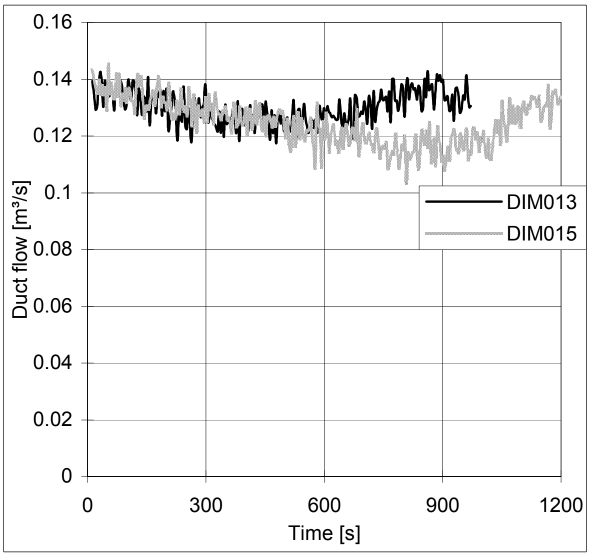


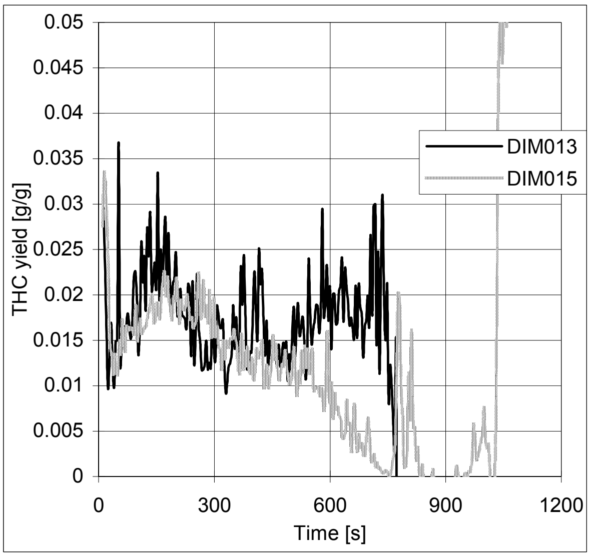


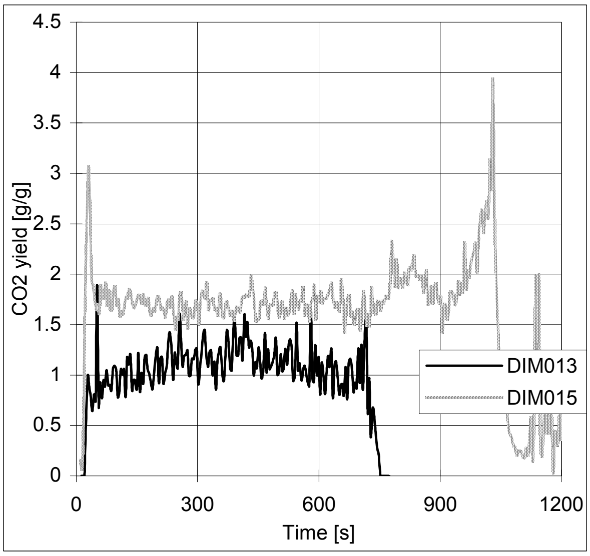


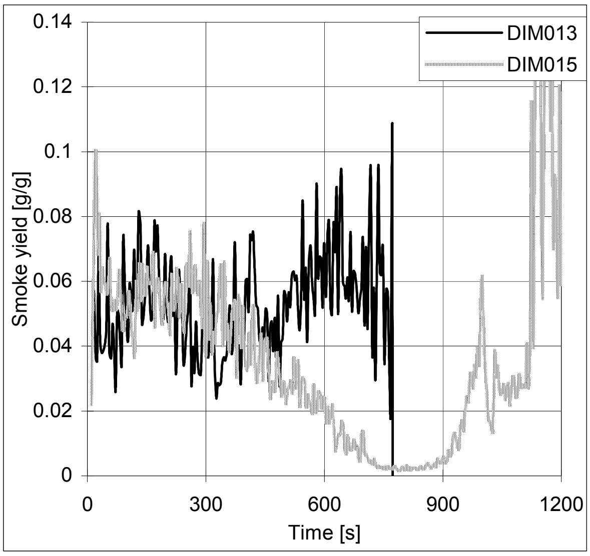


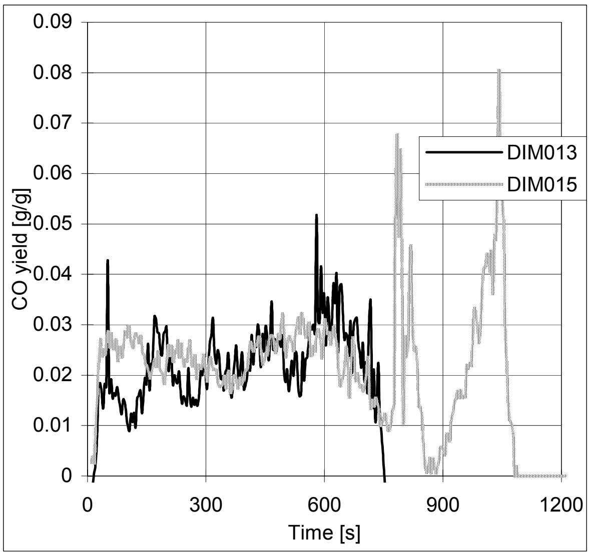


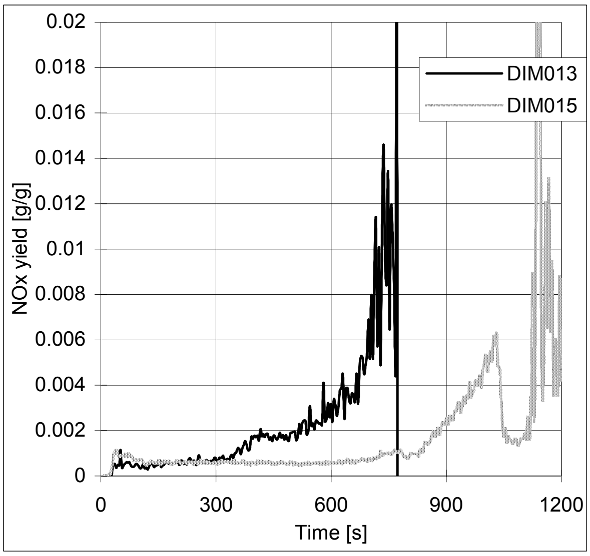

Duct flow [m³/s]
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
300
600
900
1200
Time [s]
DIM013
DIM015

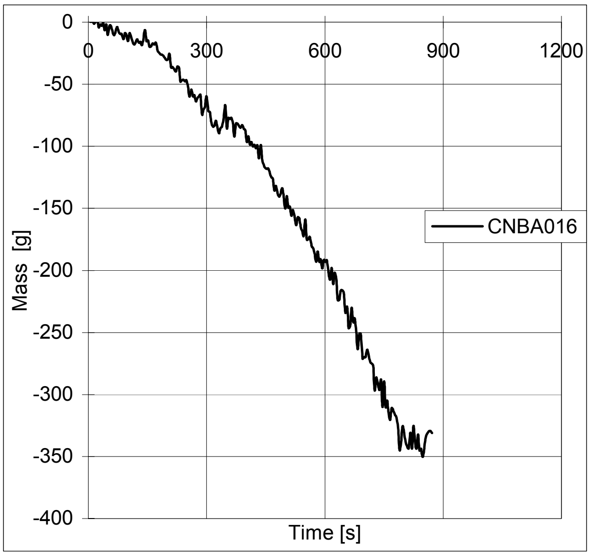

THC yield [g/g]
0.05
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
300
600
900
1200
Time [s]
DIM013
DIM015

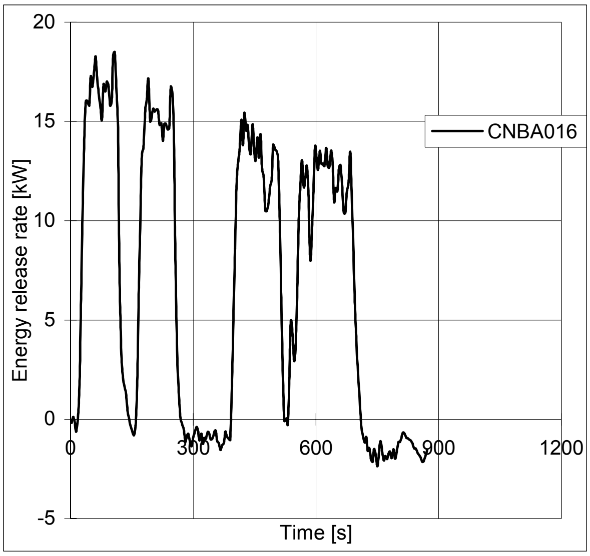

CO2 yield [g/g]
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
300
600
900
1200
Time [s]
DIM013
DIM015

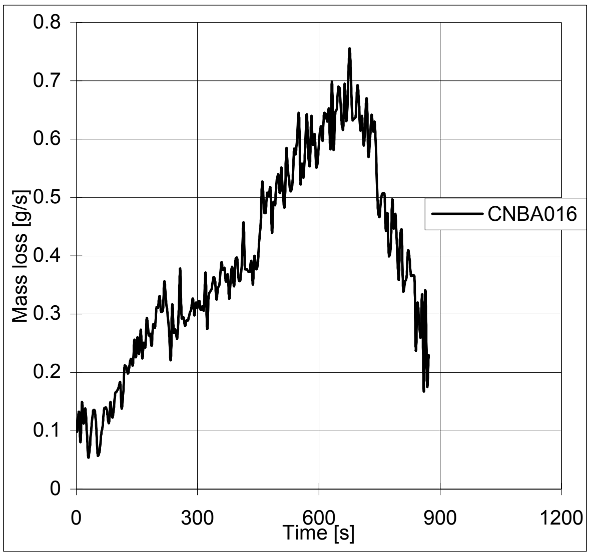

Smoke yield [g/g]
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
300
600
900
1200
Time [s]
DIM013
DIM015

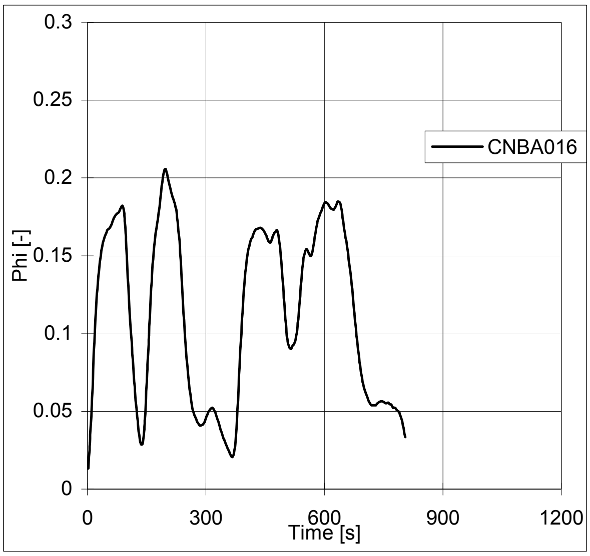

CO yield [g/g]
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
300
600
900
1200
Time [s]
DIM013
DIM015

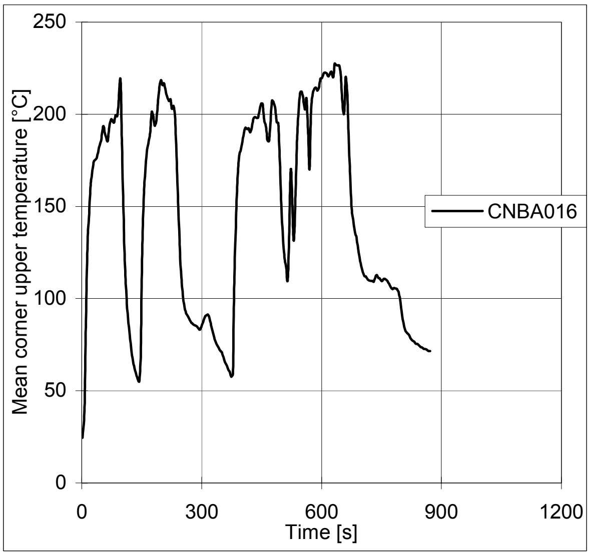

NOx yield [g/g]
0.02
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0
300
600
900
1200
Time [s]
DIM013
DIM015

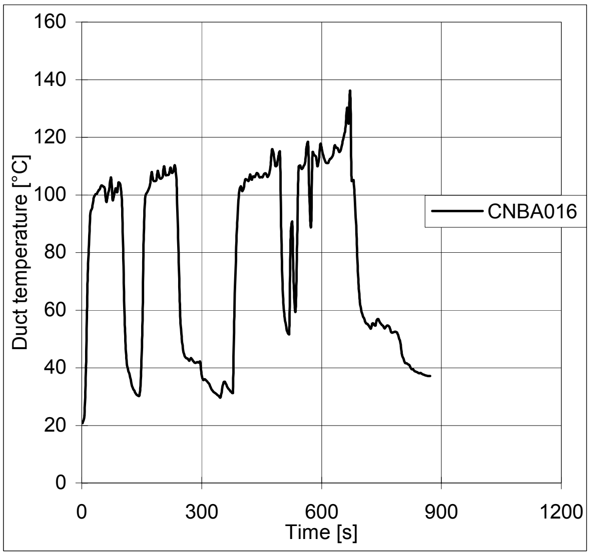

0
-50
-100
-150
-200
-250
-300
-350
-400
Mass [g]
0
300
600
900
1200
Time [s]
CNBA016

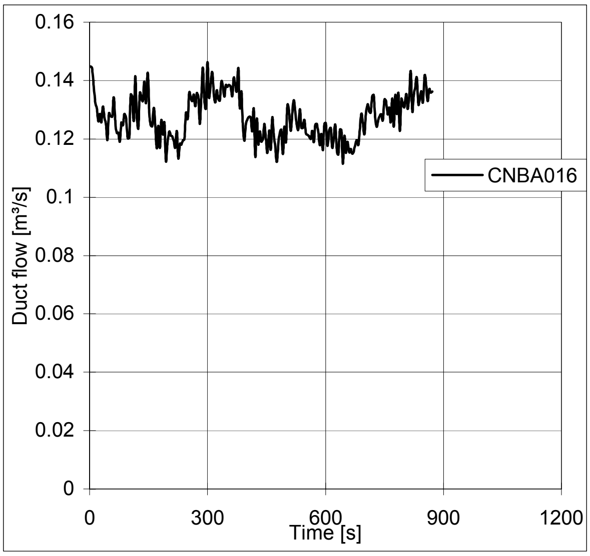

20
15
10
5
0
-5
Energy release rate [kW]
0
300
600
900
1200
Time [s]
CNBA016

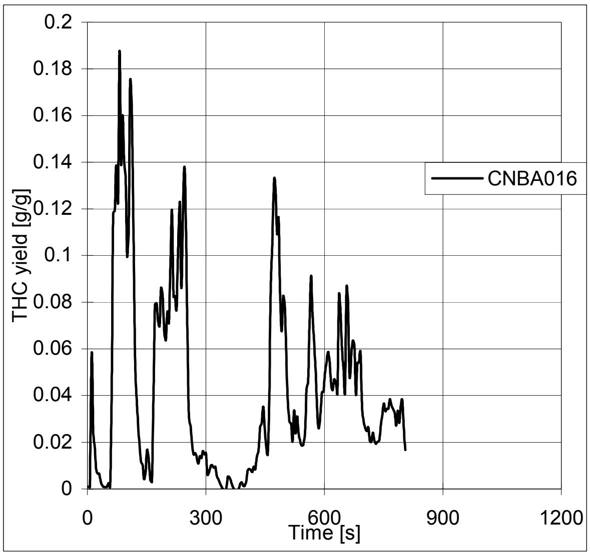

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Mass loss [g/s]
0
300
600
900
1200
Time [s]
CNBA016

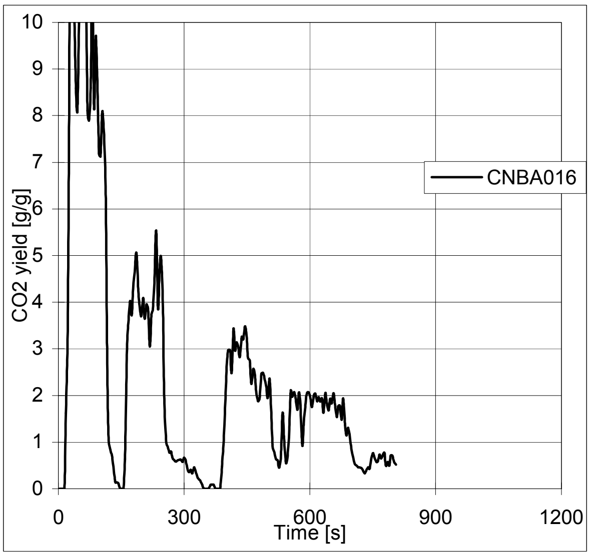

0.3
0.25
0.2
0.15
0.1
0.05
0
Phi [-]
0
300
600
900
1200
Time [s]
CNBA016

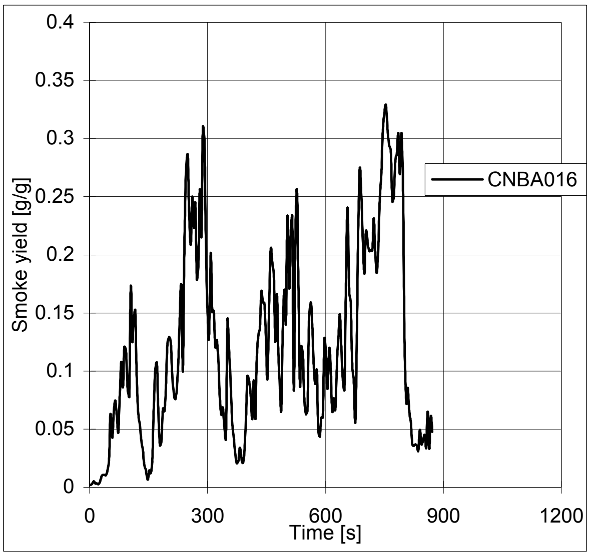

250
200
150
100
50
0
Mean corner upper temperature [°C]
0
300
600
900
1200
Time [s]
CNBA016

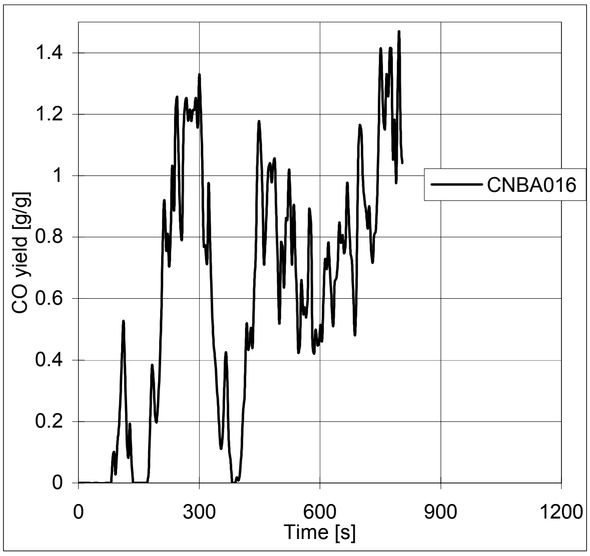

160
140
120
100
80
60
40
20
0
Duct temperature [°C]
0
300
600
900
1200
Time [s]
CNBA016

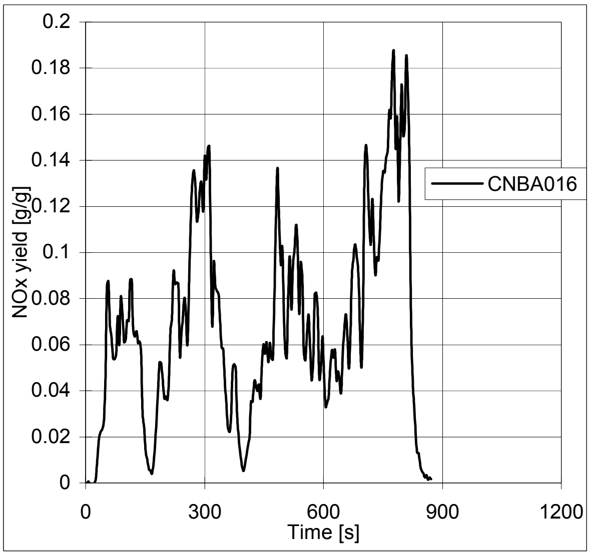

Duct flow [m³/s]
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
300
600
900
1200
Time [s]
CNBA016


THC yield [g/g]
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
300
600
900
1200
Time [s]
CNBA016

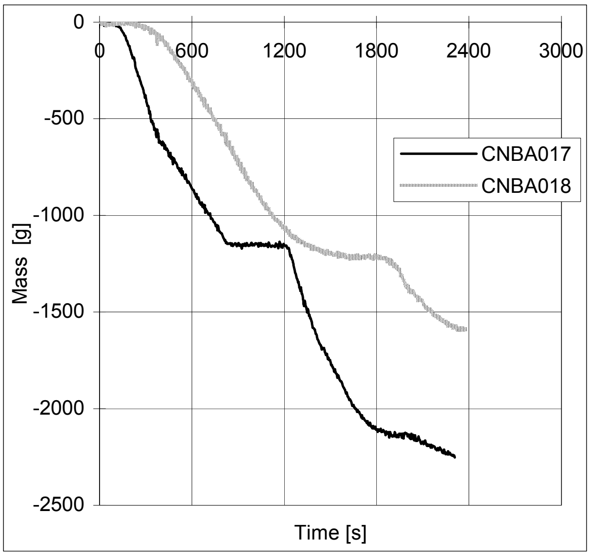

CO2 yield [g/g]
10
9
8
7
6
5
4
3
2
1
0
0
300
600
900
1200
Time [s]
CNBA016

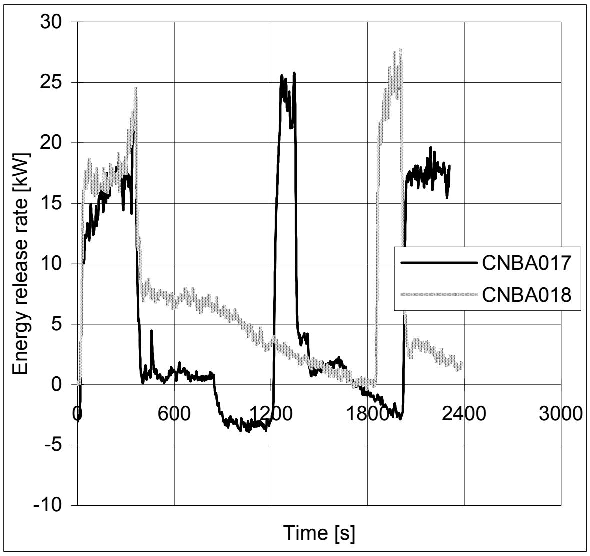

Smoke yield [g/g]
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
300
600
900
1200
Time [s]
CNBA016

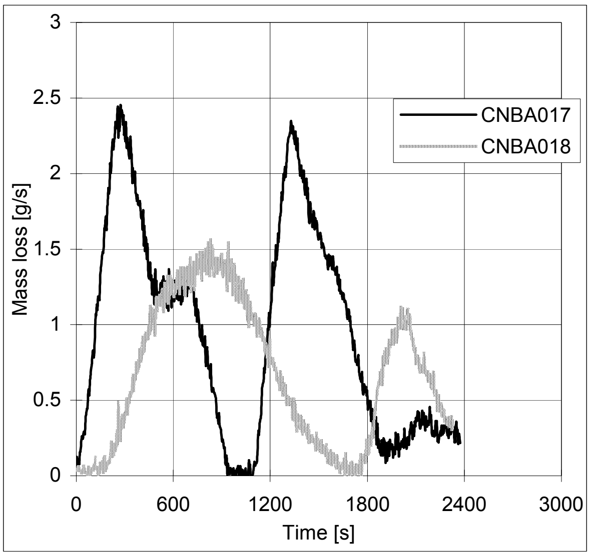

CO yield [g/g]
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
300
600
900
1200
Time [s]
CNBA016

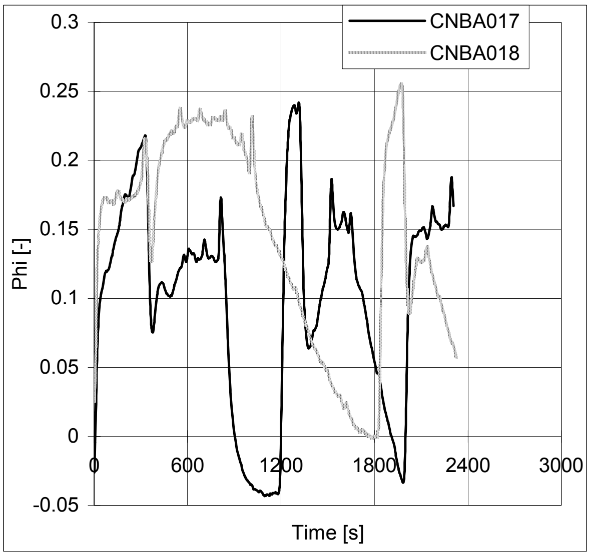

NOx yield [g/g]
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
300
600
900
1200
Time [s]
CNBA016

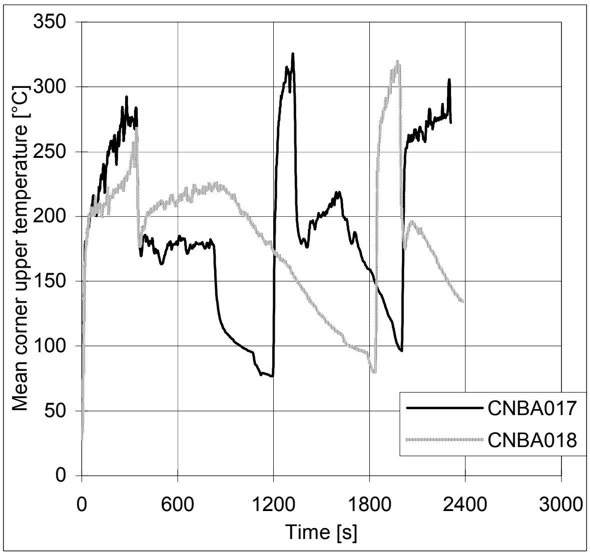
Appendix: CNBA

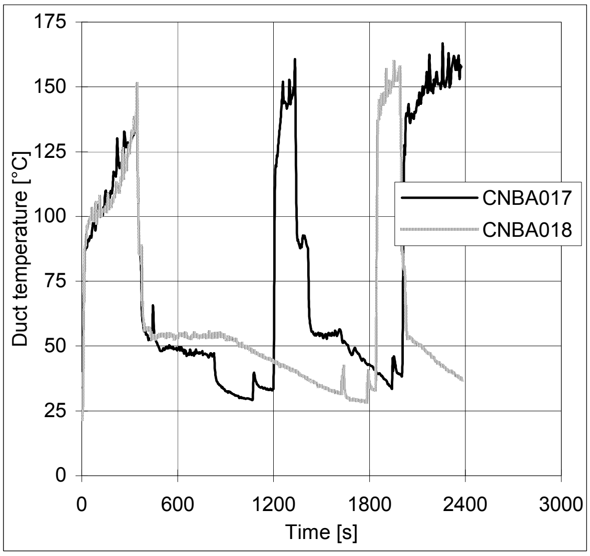


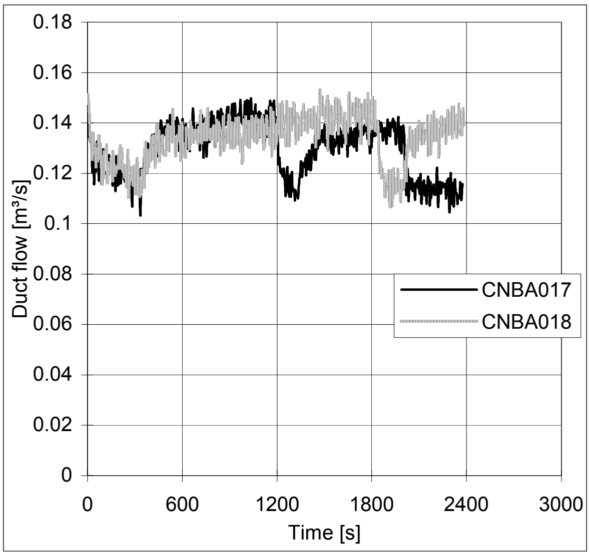


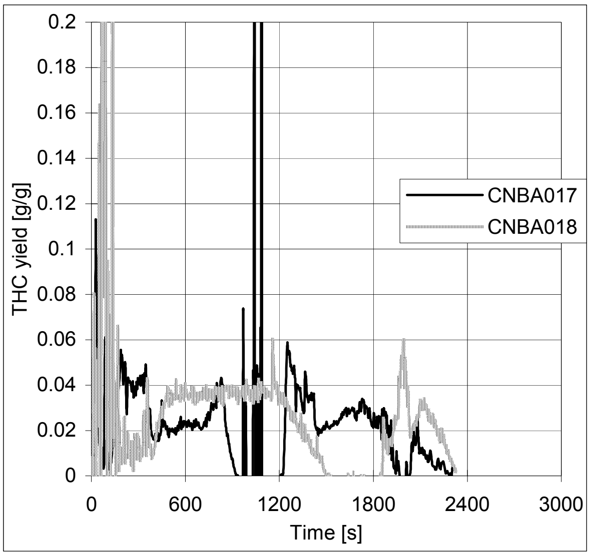


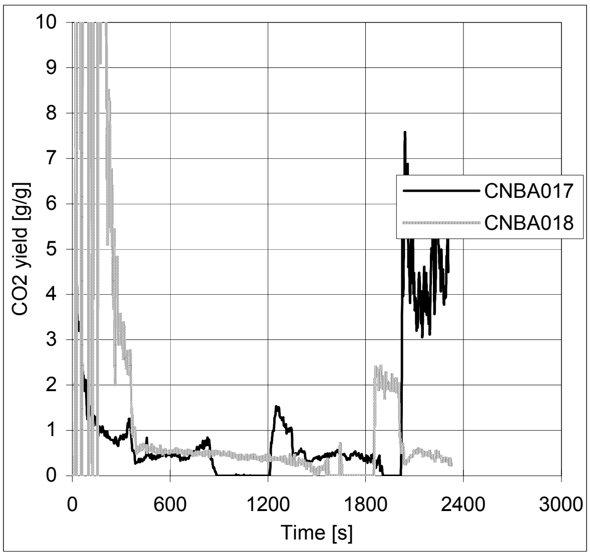


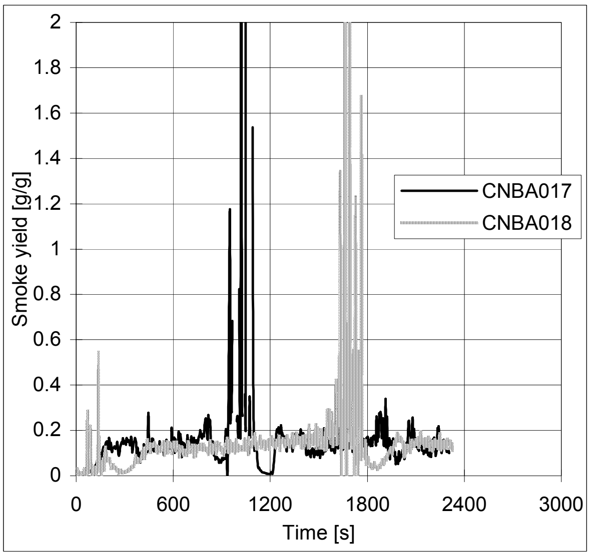


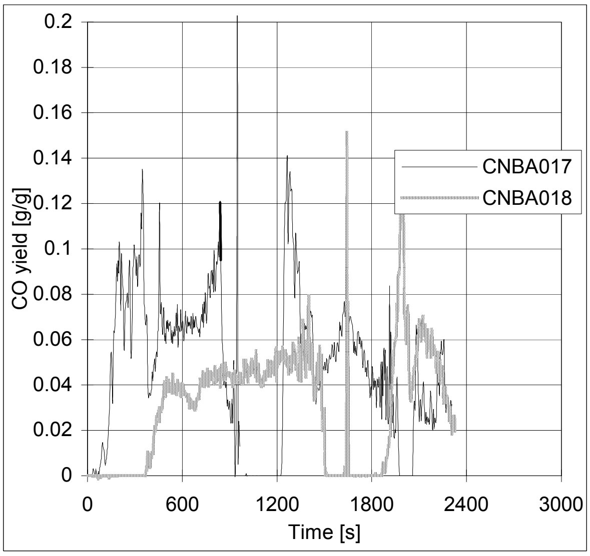


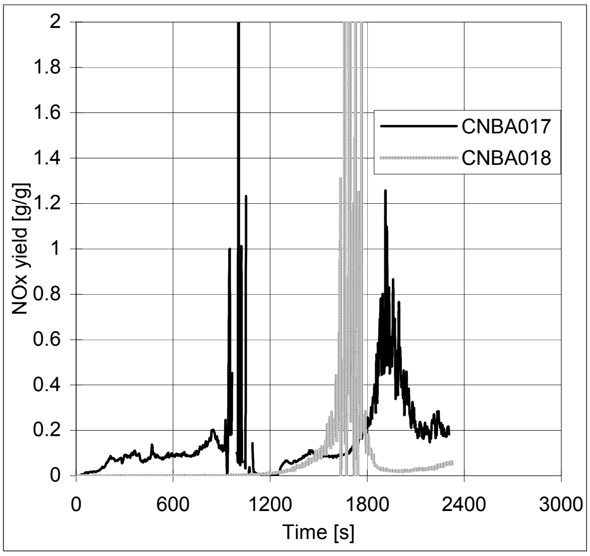

Duct flow [m³/s]
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
600
1200
1800
2400
3000
Time [s]
CNBA017
CNBA018


THC yield [g/g]
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
600
1200
1800
2400
3000
Time [s]
CNBA017
CNBA018

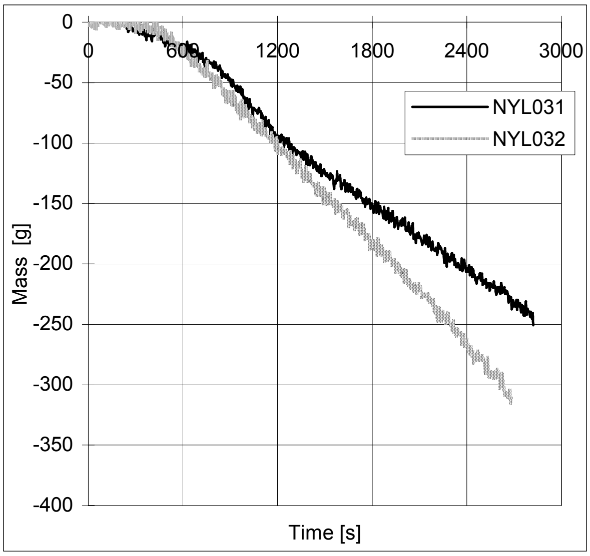

CO2 yield [g/g]
10
9
8
7
6
5
4
3
2
1
0
0
600
1200
1800
2400
3000
Time [s]
CNBA017
CNBA018

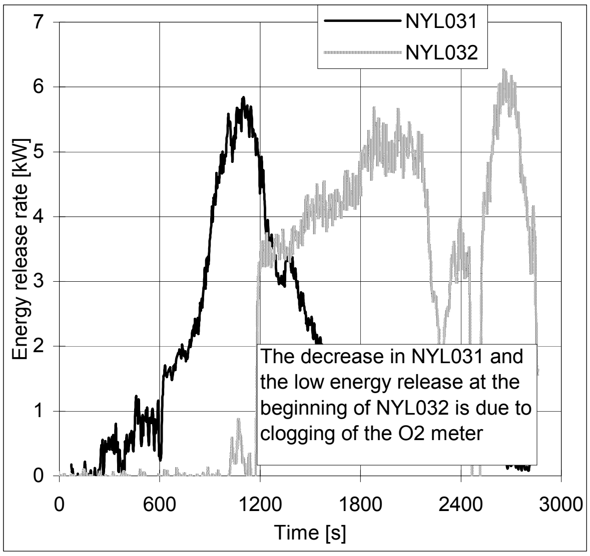

Smoke yield [g/g]
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
600
1200
1800
2400
3000
Time [s]
CNBA017
CNBA018


CO yield [g/g]
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
600
1200
1800
2400
3000
Time [s]
CNBA017
CNBA018

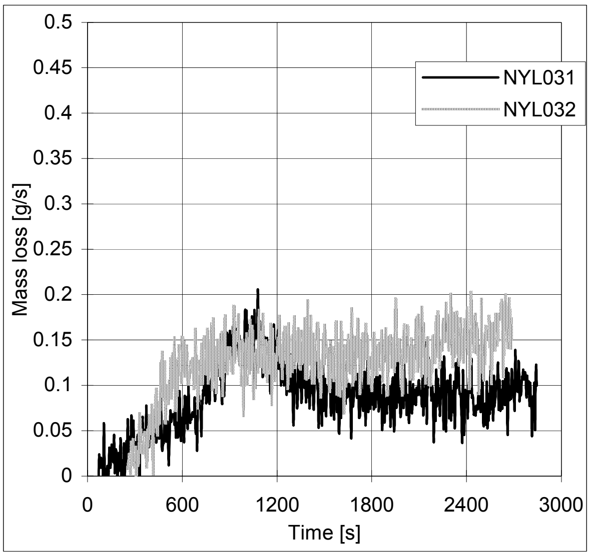

NOx yield [g/g]
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
600
1200
1800
2400
3000
Time [s]
CNBA017
CNBA018

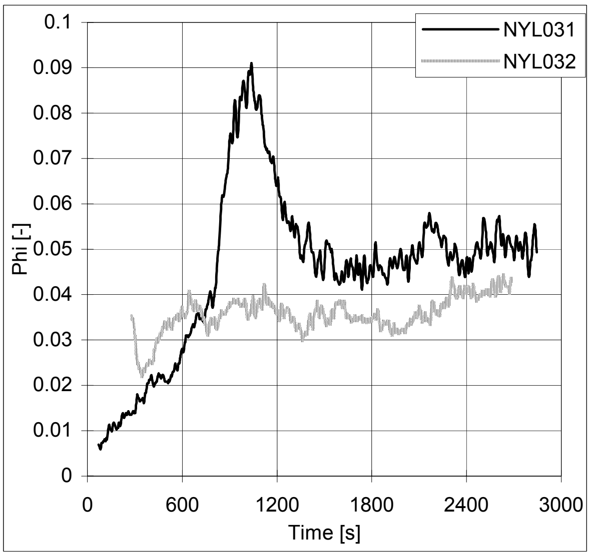
Appendix: Nylon

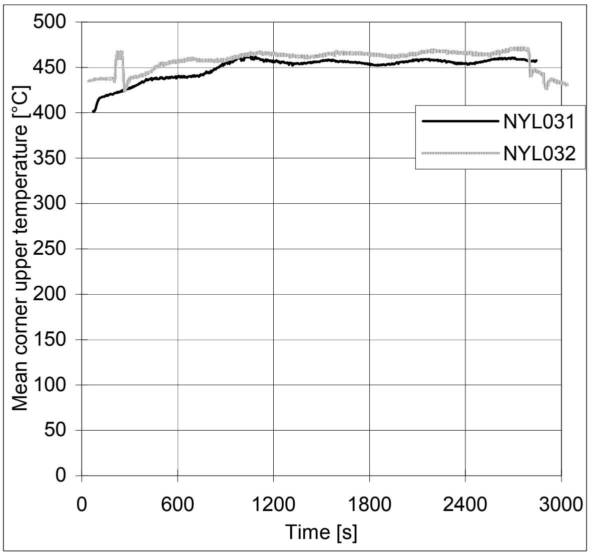


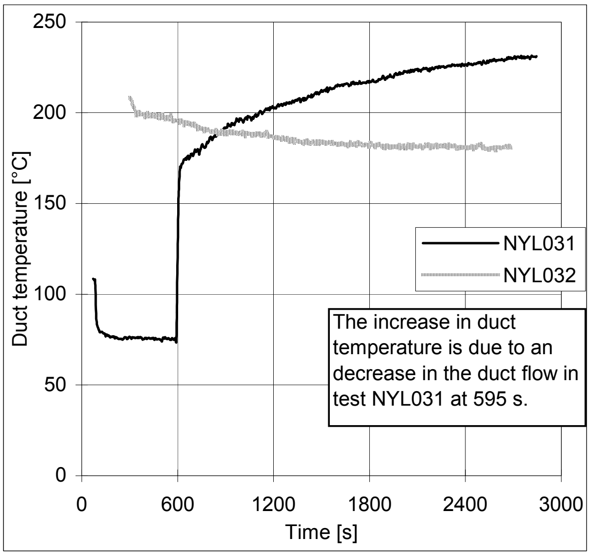


The decrease in NYL031 and the low energy release at the beginning of NYL032 is due to clogging of the O2 meter



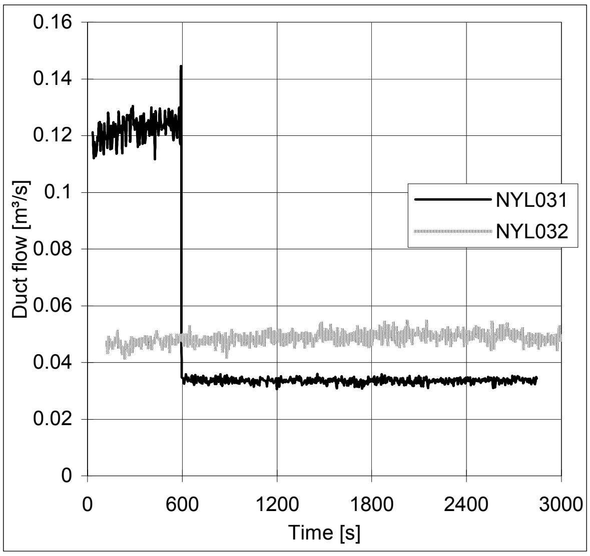


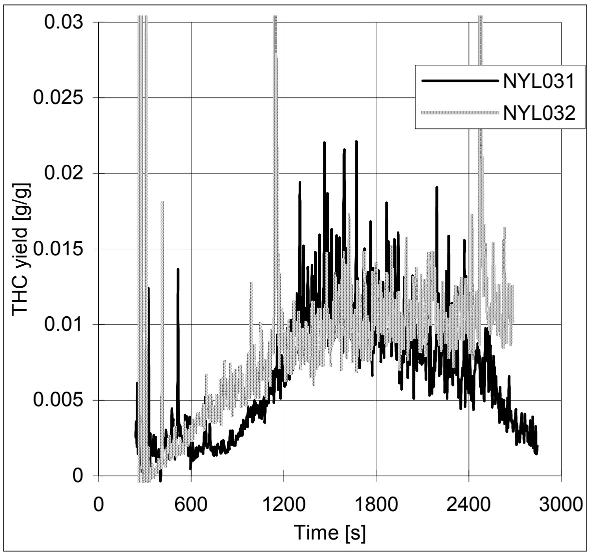


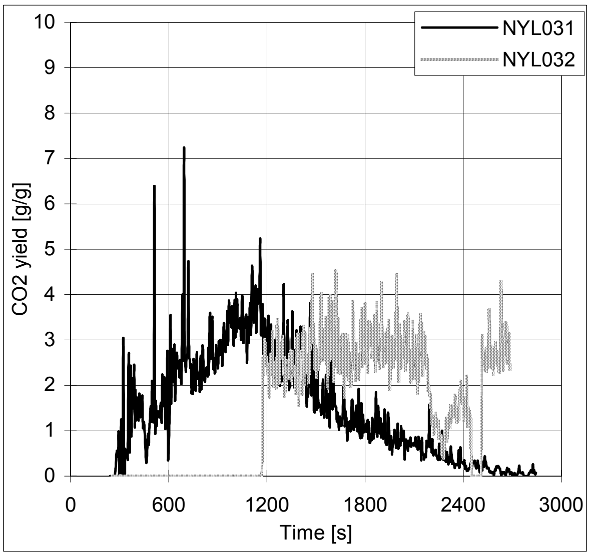


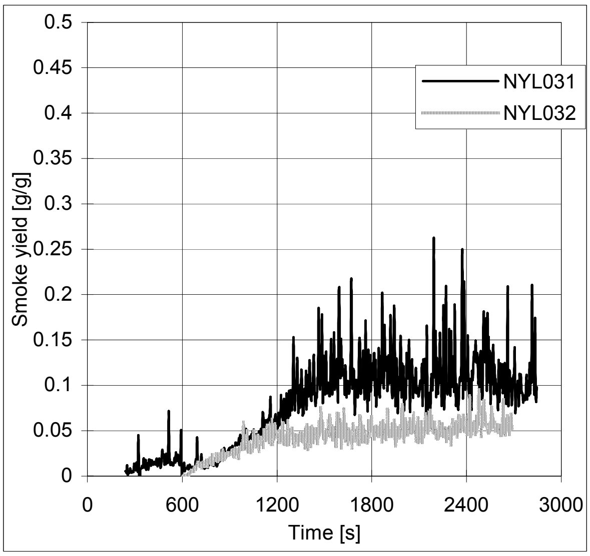
The increase in duct temperature is due to an decrease in the duct flow in test NYL031 at 595 s.

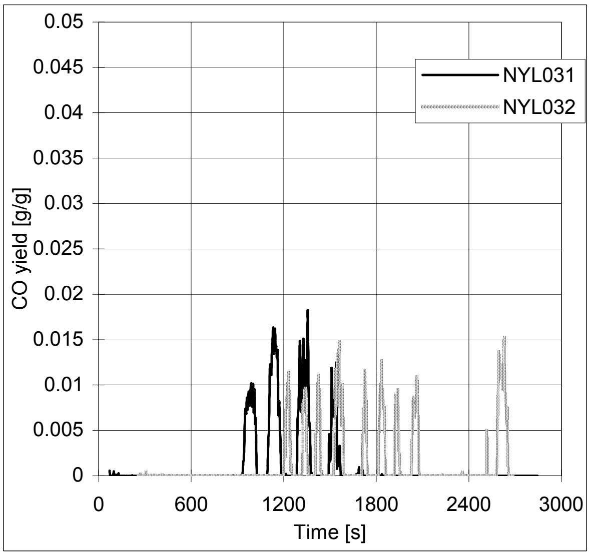
Appendix: Nylon

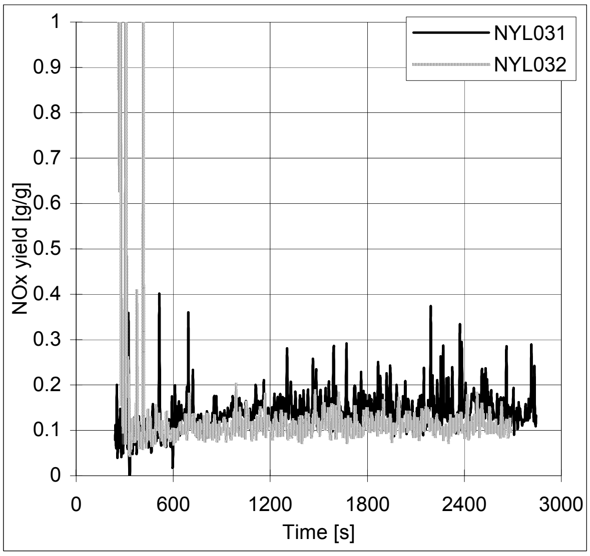




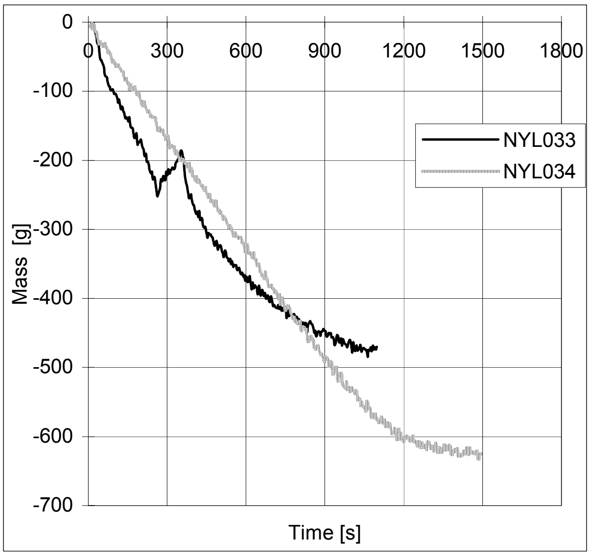


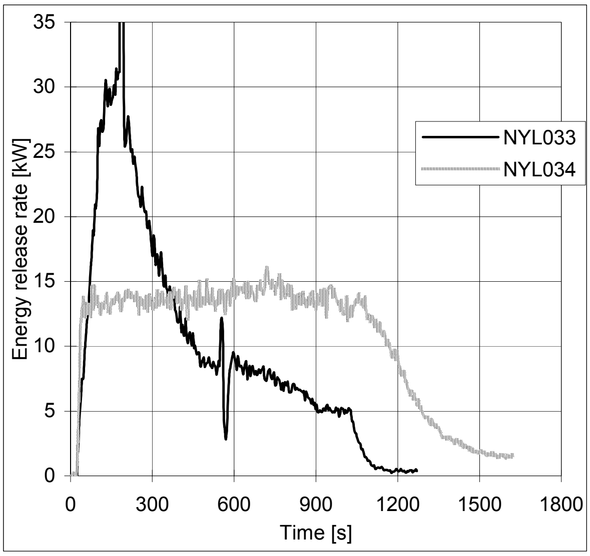


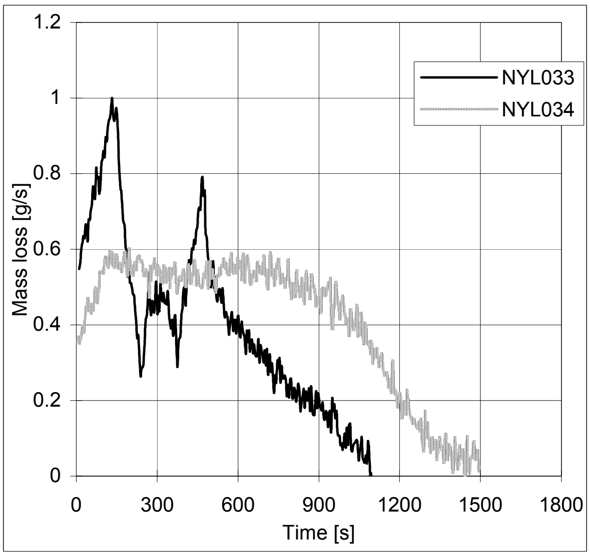


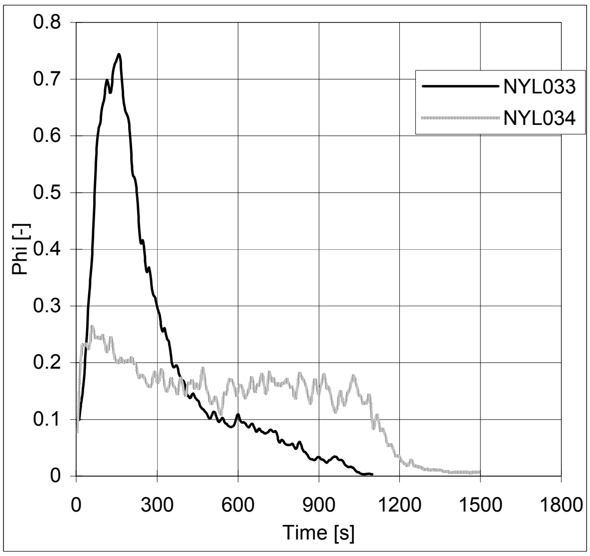


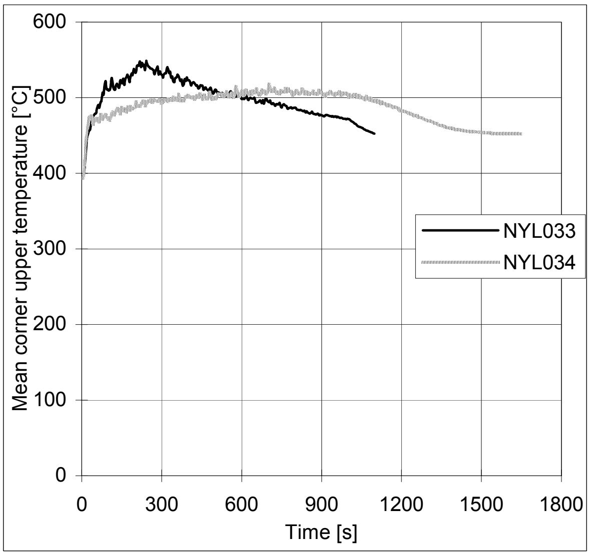
Appendix: Nylon

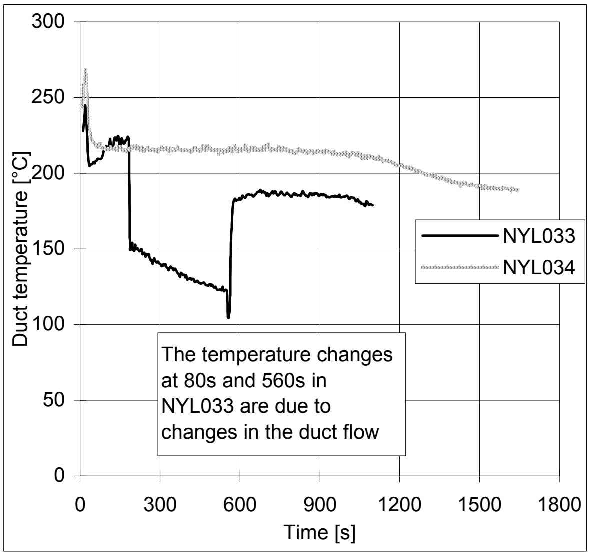




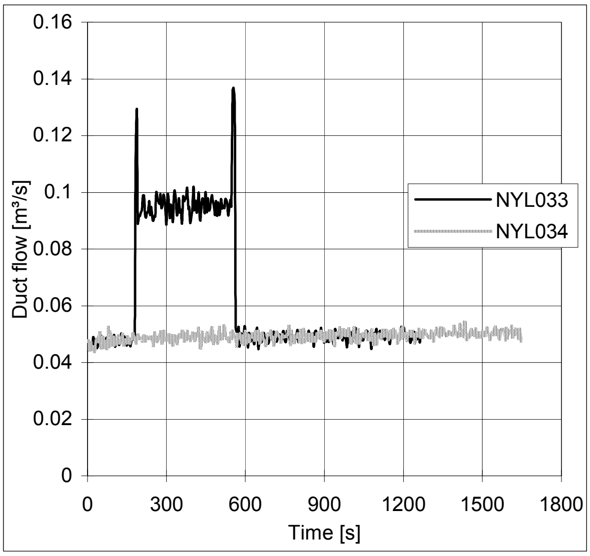


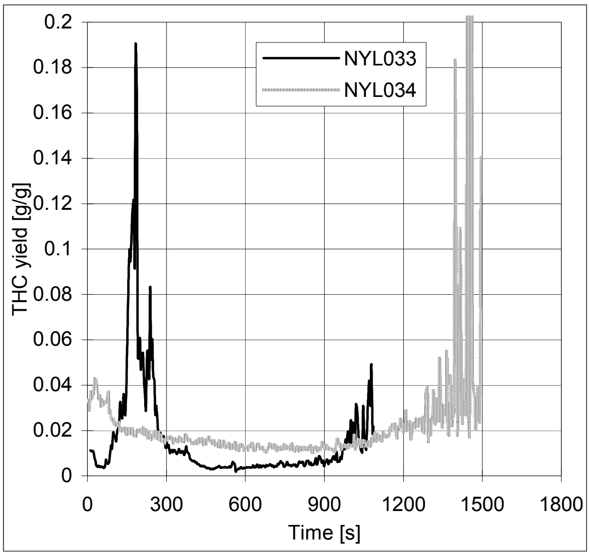


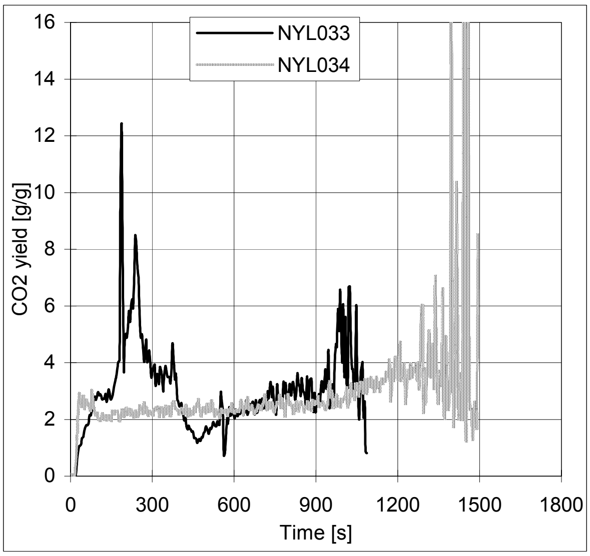


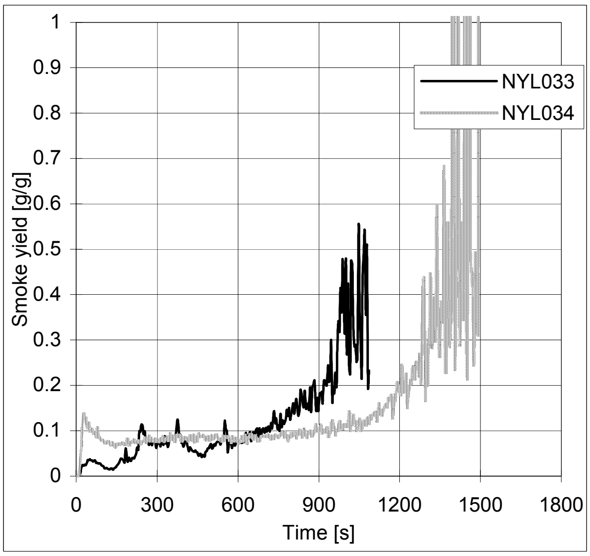


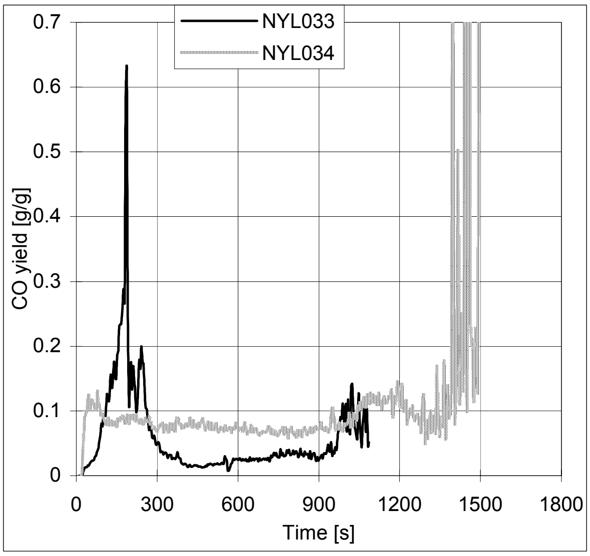
The temperature changes at 80s and 560s in NYL033 are due to changes in the duct flow

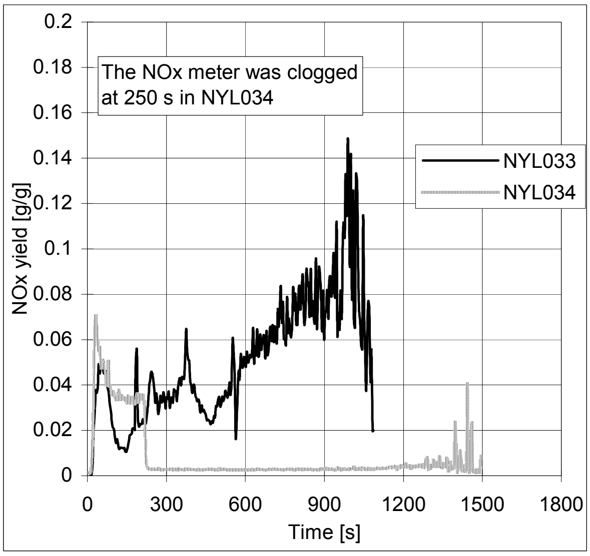






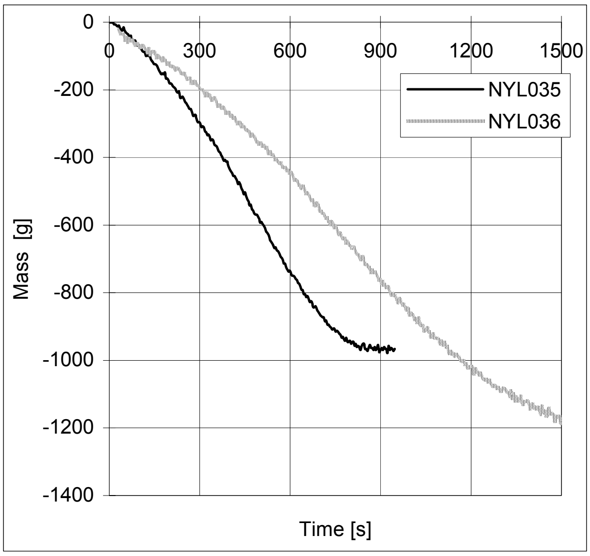


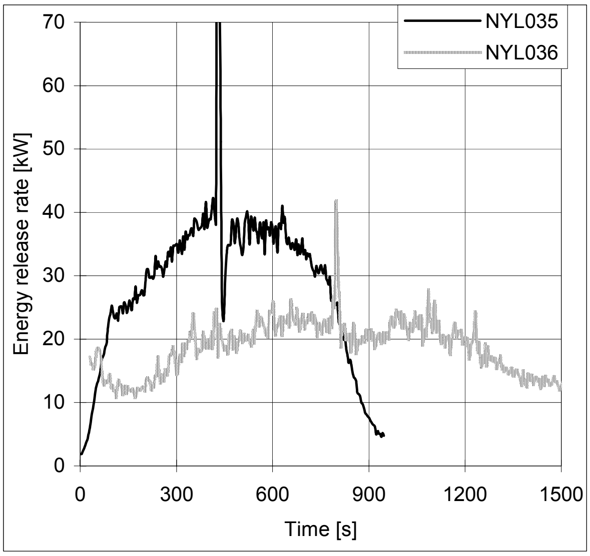


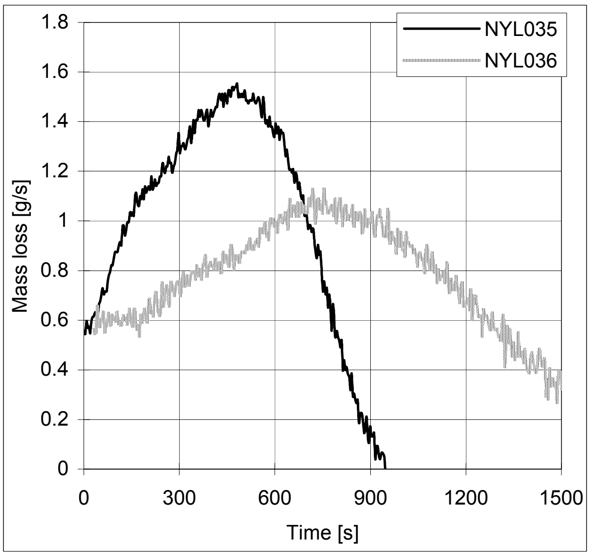


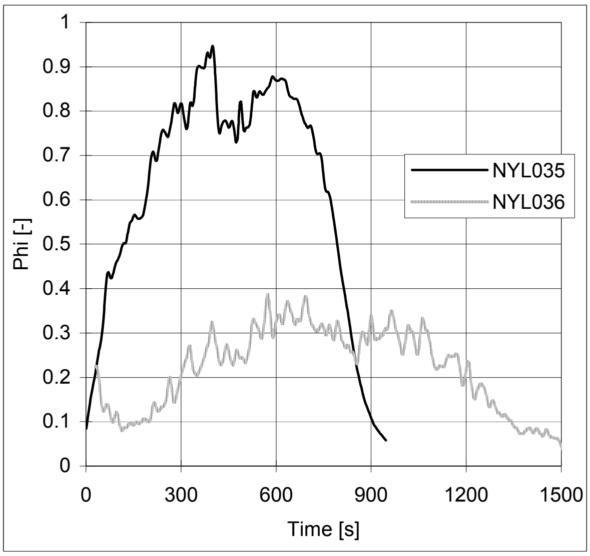
The NOx meter was clogged at 250 s in NYL034

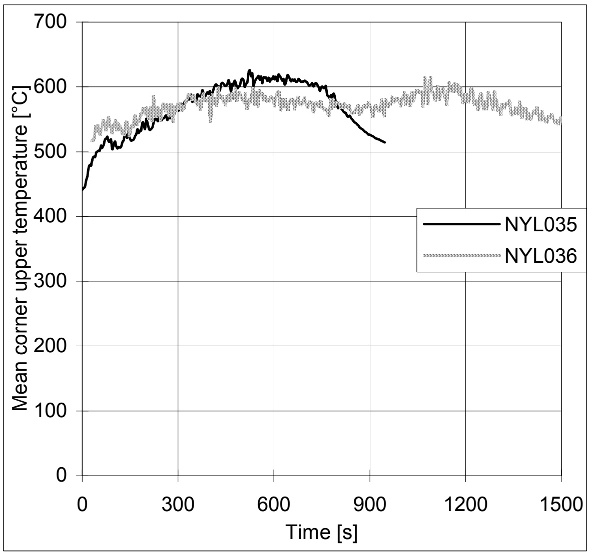
Appendix: Nylon

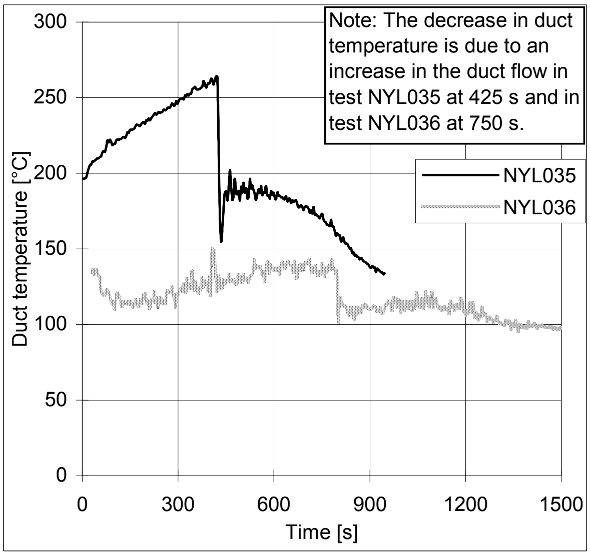






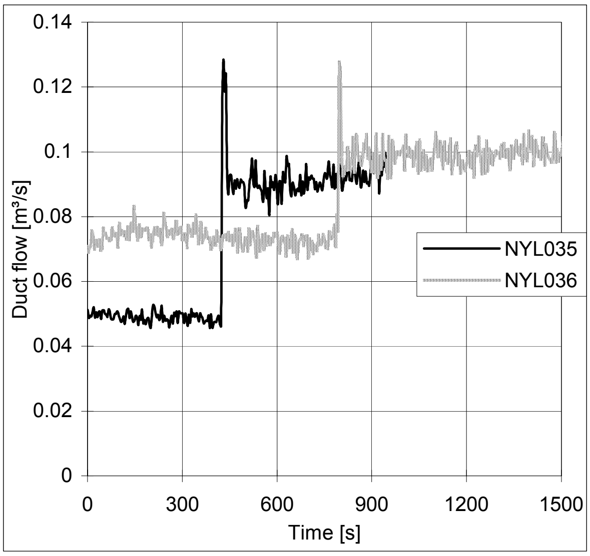


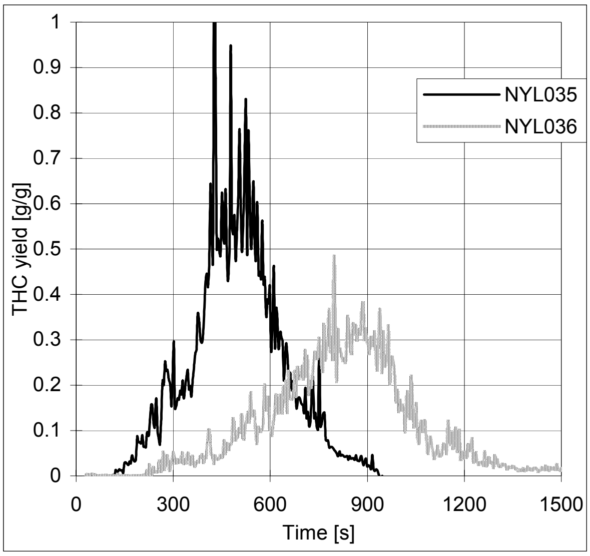


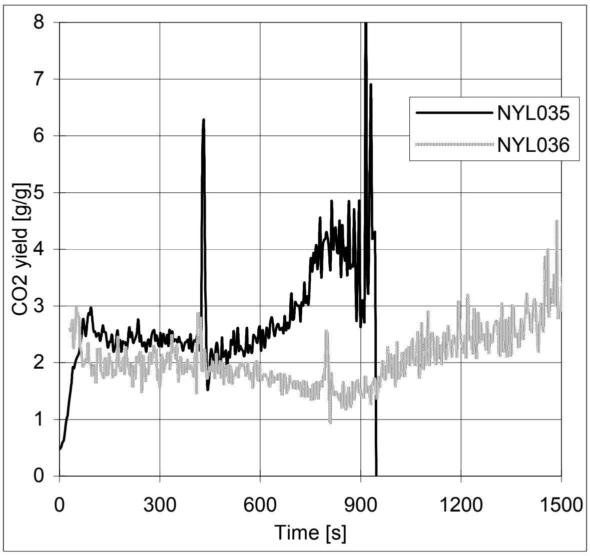


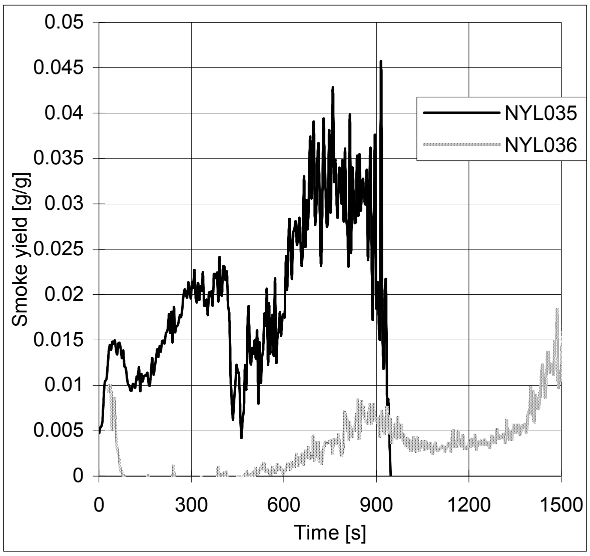
Note: The decrease in duct temperature is due to an increase in the duct flow in test NYL035 at 425 s and in test NYL036 at 750 s.

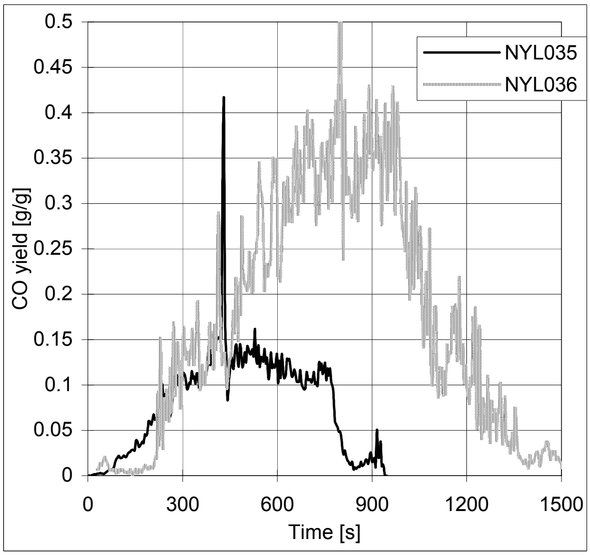
Appendix: Nylon

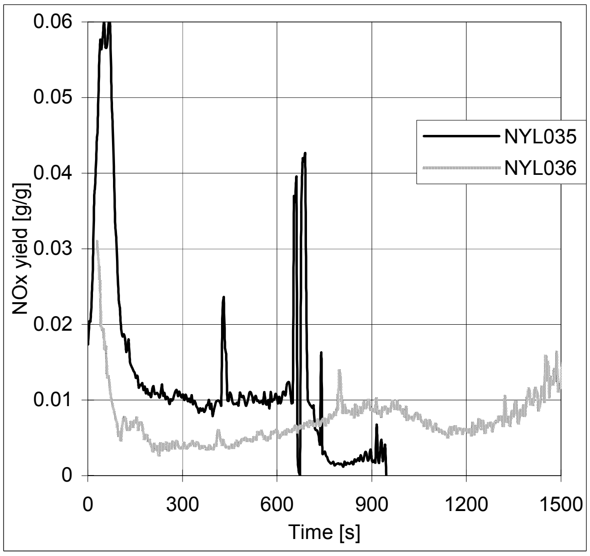












Combustion products generated by hetero-organic fuels on four different fire test scales

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Abstract

The scaling of results from combustion experiments with four organic substances containing heteroatoms, carried out on four different scales, is discussed. The scales ranged from the micro-scale, using about $2 \cdot 10^{-3}$ kg of the substances, to large scale using about 50 kg of the substances. The content of O_2, CO, CO_2, NO_x, HCl, HCN and SO_2 in the combustion gases were determined with special attention to the survival fractions of the tested substances and the amount of unburned hydrocarbons. The Global Equivalence Ratio (GER) was used to describe the ventilation conditions during the experiments. The conditions were adjusted to range from under- to well-ventilated situations. It was found that the GER is not the only parameter that influences the production of combustion gases. Other parameters such as temperature and residence time also seem to be important in explaining the results. The experiments were performed as a part of the TOXFIRE project within the EC Environment programme.

Keywords: Scaling, combustion products, survival fractions, ventilation, global equivalence ratio, GER

1. Introduction

Fires in chemical warehouses are a potential danger to people on the premises or in the vicinity and to the environment. A number of major accidents have already occurred, e.g. the Sandoz fire in Basle, Switzerland in 1986. A lack of knowledge concerning such hazards was recognised and therefore projects were initiated by the European Commission (EC) to improve the situation. One of the projects was entitled TOXFIRE, ”Guidelines for Management of Fires in Chemical Warehouses”. The EC Environment Programme funded the project, which was carried out by organisations from a number of European countries. The consortium involved Denmark (Risø National Laboratory, the Danish National Environmental Research Institute), Sweden (Lund University, the Swedish National Testing and Research Institute, the Swedish National Defence Research Establishment), Finland (the Technical Research Centre of Finland) and Great Britain (South Bank University) with Risø National Laboratory as the co-ordinator. An overview of the whole project is given in [1, 2]. In the following the results of the TOXFIRE project dealing with scaling effects are presented.

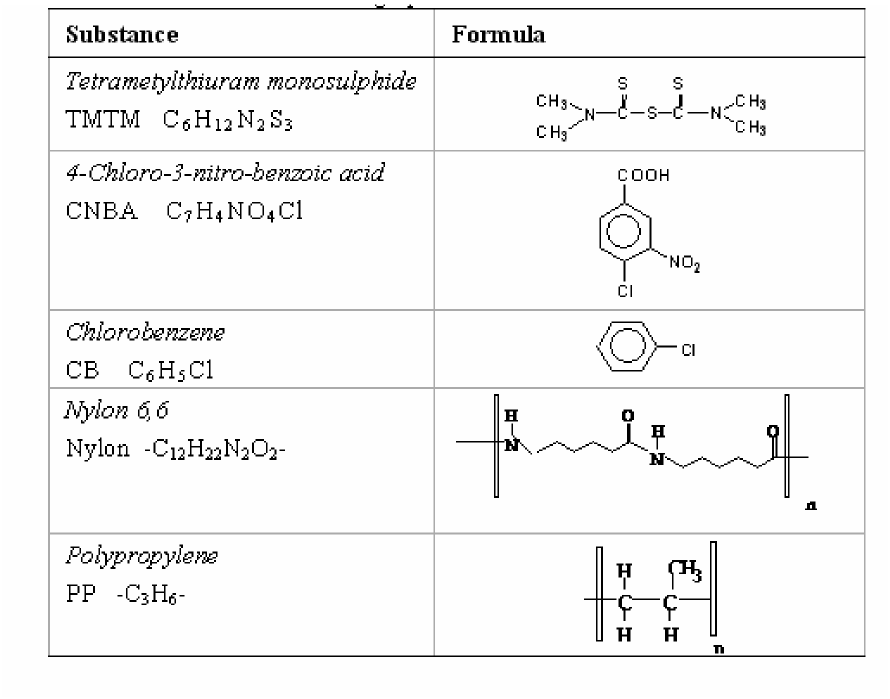
2. Scaling

A chemical warehouse fire is likely to occur in a building, vastly larger than an ISO test room. Unfortunately, it is economically impossible to study a fire under controlled conditions on such a large scale. Therefore, it is necessary to employ scaling in order to obtain the relevant fire-fighting information. Thus, a methodology must be established for determining combustion properties based on small-scale tests, which can then be translated into real-life scales. In the experiments presented here four different scales were employed, including micro, small, medium and large scale.

The combustion set-ups used were a tubular furnace, “DIN furnace” method [3, 4] (1-$3 \cdot 10^{-3}$ kg fuel), a cone calorimeter, “cone calorimeter”[5] ($10\text{-}20 \cdot 10^{-3}$ kg fuel), a medium-scale room facility, “1/3 ISO room” [6], (0.5-1 kg fuel) and an ISO room, “ISO room” [7] (50 kg fuel). Thus the scaling factors expressed, as the fuel ratios were 1:10:500:50,000. The substances were burned under different fire conditions and the combustion products, including the survival fractions, were analysed. The ventilation conditions were characterised using a ϕ-meter [8] in the 1/3 ISO room and the ISO room. In the other set-ups the ϕ-value had to be calculated.

Tests were carried out with four chemicals containing the heteroatoms, N, S and Cl, Table 1. Tetramethylthiuram monosulphide (TMTM) is used in vulcanising processes in the rubber industry and is a compound with the heteroatoms N and S. It was used in the form of yellow granules. 4-Chloro-3-nitro-benzoic acid (CNBA), which is used in dye production, contains N and Cl and is a white powder. Chlorobenzene (CB) is a liquid solvent containing Cl. Two polymers nylon 6,6 (nylon) and polypropylene (PP) were also included. Nylon contains N whereas PP consists solely of C and H and was included as a reference material. Both polymers were in the form of pellets.

Table 1: Substances used in the scaling experiments



Substance	**Formula**
Tetrametylthiuram monosulphide TMTM $C_6H_{12}N_2S_3$	
4-Chloro-3-nitro-benzoic acid CNBA $C_7H_4NO_4Cl$	
Chlorobenzene CB C_6H_5Cl	
Nylon 6,6 Nylon $-C_{12}H_{22}N_2O_2-$	
Polypropylene PP $-C_3H_6-$	

3. Determination of GER

The type of fires considered take place in enclosed spaces. The influence of the degree of ventilation is therefore of special interest. One way of describing the ventilation conditions in a fire is to use the global equivalence ratio, GER, often denoted by the Greek letter ϕ, defined as:

$$\phi = \frac{\dot{m}_{fuel} / \dot{m}_{oxygen}}{\left(\dot{m}_{fuel} / \dot{m}_{oxygen}\right)_{stoich}} \qquad \text{[Eq. 1]}$$

$$\begin{aligned} &\phi = 1 \ \textit{stoichiometric combustion} \\ &\phi < 1 \ \textit{well - ventilated combustion} \\ &\phi > 1 \ \textit{under - ventilated combustion} \end{aligned}$$

The ϕ-value can be measured experimentally, using a ϕ-meter [8]. The ϕ-value can be determined from the instrument by the equation:

$$\phi = (X_{O_2} - X_m)/(X_0 \cdot (1 - X_m)) \qquad \text{[Eq. 2]}$$

In Eq. 2 X_{O_2} is the oxygen concentration before combustion, X_m is the oxygen concentration during the experiment and X_0 is the concentration of oxygen in the surrounding air, normally 20.9%. The ϕ-meter was used in the medium-scale experiments and in the ISO room set-up.

In Eq. 1 the ratio between the amount of fuel, $\dot{m}_{fuel}$ and the actual oxygen concentration, $\dot{m}_{oxygen}$ is compared to the same ratio at stoichiometric conditions. The GER can also be calculated by measuring the mass loss of the burned substance and the volume of air that enters the combustion chamber. In [9] Babrauskas has presented an expression by which the GER for a fire in an enclosure can be estimated. The flow of air into a fire enclosure can be expressed as in equation 6.19 in [9] here given as Eq.3, based on work presented in [10].

$$\dot{m}_{air} = \frac{2}{3} \cdot C_d \cdot B_v (h_0)^{3/2} \cdot \rho_0 \cdot \sqrt{2 \cdot g \cdot (1 - \frac{\rho_0}{\rho_f})} \qquad \text{[Eq. 3]}$$

In Eq.3 $\dot{m}_{air}$ is the flow of air into the enclosure, C_d is a discharge coefficient, B_v is the width of the opening, h_0 is the height of the opening up to the neutral plane. ρ_0 is the density of the surrounding air and ρ_f is the density of the combustion gases leaving the enclosure. The density of the combustion gases, ρ_f, flowing out of the compartment is of course dependent of the composition of the combustion products but a large part of the gas flow is nitrogen so the assumption is made that the molecular weight of the gases coming out of the enclosure is the same as for the air flowing in. The symbol g is the standard gravity. The position of the neutral plane can be determined by equation 6.20 in [9] here presented as Eq. 4.

$$h_0 = \frac{h_v}{1+\left(\frac{\rho_0}{\rho_f}\cdot\left(1+\frac{\phi}{r}\right)^2\right)^{1/3}} = \frac{h_v}{1+\left(\frac{T_f}{T_0}\cdot\frac{W_0}{W_f}\cdot\left(1+\frac{\phi}{r}\right)^2\right)^{1/3}} \qquad \text{[Eq. 4]}$$

In Eq. 4 h_v is the total height of the opening and r is the stoichiometric air/fuel mass ratio. T_f is the temperature of the combustion gases and T_0 is the temperature of the surrounding air. W_f is the molecular weight of the combustion gases and W_0 is the molecular weight of air. It is assumed that the mass flow of air into the enclosure is equal to the outflow of gases by introducing the approximation that $\frac{\phi}{r}\rightarrow 0$ which gives Eq. 5 below, rewritten from an equation presented by Babrauskas in [9].

$$\phi = \frac{\dot{m}_{fuel}\cdot\left(1+\left(\frac{T_f}{T_0}\right)^{1/3}\right)^{3/2}}{\frac{2}{3}\cdot(h_v)^{3/2}\cdot w\cdot C_d\cdot\sqrt{2\cdot g}\cdot\rho_0\cdot\left(1-\frac{T_0}{T_f}\right)^{1/2}\cdot r} \qquad \text{[Eq. 5]}$$

The discharge coefficient C_d was by Kawagoe [11] found to range between 0.5 and 1.0 and Steckler et. al. [12] gave it a value of 0.7. For the set up used in the medium scale experiments the value of 0.68 for the discharge coefficient presented in [13] by Prahl and Emmons was found suitable. The approximation $\frac{\phi}{r}\rightarrow 0$ gives an error of around 3-4 % for ϕ = 1 up to an error of 10% for ϕ = 3 for propane with an r = 15.6. This was deemed acceptable. Eq. 5 was used only as a means of verifying the results from the ϕ-meter for the experiments in medium-scale.

4. Experimental equipment and procedures

Experiments are presented from four different experimental set-ups, which are presented below. These set-ups have a considerably varying layout and this might give results that are difficult to compare. One aim of the TOXFIRE project was however to compare results from these different set-ups to see whether it was possible to use results from relatively small scale experiments for hazard analysis.

4.1 DIN furnace set-up

The micro-scale experiments [14] were carried out according to methods described in references [3, 4]. The experimental set-up is shown in Fig. 1a. The studied substance was placed in a quartz boat containing small ceramic vessels and the mass of the sample was determined prior to start of the experiment. The mass of the substance, which remained after the experiment, was also measured. The mass loss was estimated from these masses and from the combustion times for each vessel. The times where taken from the FTIR spectra. The mass loss was then given as a mean value for the whole experiment.

The tests were performed under two different furnace temperatures (500 °C and 900 °C) and three different airflow conditions (100 l/h, 50 l/h and 50 l air/h mixed with 50 l nitrogen/h) in order to simulate different fire conditions using the ISO classification [15, 16]. The chosen airflow conditions gave GER values of 0.5, 0.7 and 1.1 respectively. In these experiments on-line gas analysis with FTIR was made to quantify combustion gases such as CO_2, CO, HCN, NO_x, SO_2 and HCl. Off-line GC/MS analysis was also used to determine the presence of organic combustion products. Experiments were performed with all the substances except PP.

The DIN furnace is kept at a chosen temperature and the substance, which is of ambient temperature, is introduced and the furnace slowly moves along the vessels with substance. This means that the temperature will vary during an experiment since the substance is relatively cold at the beginning but is then heated by the furnace. Pyrolisation and degradation will start and for most of the substances combustion will take place. Whether the combustion is flaming or not is not possible to determine.

4.2 Cone calorimeter set-up

Experiments were performed on a small scale in an apparatus referred to as a cone calorimeter [5]. In the experiments a modified, ventilation-controlled cone calorimeter, was used [17, 18], see Fig. 1b. The sample and the load cell were placed in an enclosure in which the amount of oxygen available for combustion could be varied by adjusting the flow rates of the input gases and/or their oxygen concentration. In the set-up used here, the air and nitrogen flow rates could be adjusted between 0.5 and 4.0 l/s, this gave GER values from 0.2 to 2.9. In the cone calorimeter the composition of the combustion gases, CO_2, CO, NO_x, HCN, SO_2 and HCl, was determined on-line with FTIR. High molecular weight components in the combustion gases were analysed off-line with GC/MS techniques.

The construction of the ventilation-controlled cone calorimeter makes it difficult to define the GER in an indisputable way. In some experiments substantial burning occurred outside the test chamber and in those cases the amount of oxygen available for combustion exceeds the amount of oxygen fed into the cone enclosure. This problem is thoroughly discussed by Hietaniemi et al. in [18]. Here a GER based on the mass rate of oxygen fed into the test chamber is used. This quantity is time dependent since the mass loss rate varies throughout the experiment. The mass flow of oxygen into the enclosure is however constant during the experiment. Experiments were performed in the cone calorimeter with all the substances described above.

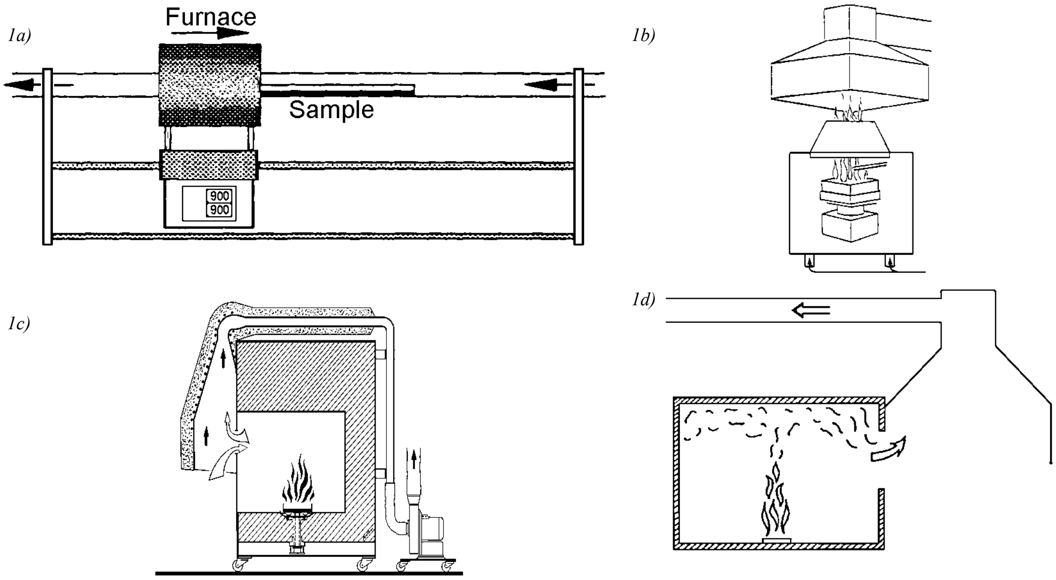


Figure 1. The experimental set-ups used: a) micro scale, a DIN furnace, b) small scale, the cone calorimeter, c) medium scale, the 1/3 ISO room and d) large scale, the ISO room.

4.3 The medium-scale room

The medium-scale combustion tests were performed in a stainless steel combustion chamber fitted inside a furnace. The internal dimensions of the chamber were 0.75 m (width), 1.1 m (depth) and 0.8 m (height), which is approximately 1/3 of the standard ISO room corner test. The opening height of the chamber was adjustable in order to allow the ventilation conditions to be changed. Two different opening configurations were used. The opening had a width of 0.45 m in all experiments but the height was varied. For most of the experiments the height was 0.2 m and it was positioned 0.125 m from the top of the enclosure. In order to study the influence of the position of the opening an arrangement with a 0.05 m opening at the bottom of the enclosure and a 0.1 m opening positioned 0.125 m from the top was also used. A GER from 0.2 to 2.0 was attained in the medium-scale experiments. These different arrangements have an influence on the flow pattern inside the enclosure and also on the residence time for the combustion gases. In some of the experiments unstable situations with pulsating fires as a result and this made it difficult to reach high ϕ-values in the medium-scale experiments.

It was possible to heat the walls and the ceiling of the chamber so that external heat could be applied. The overall configuration of the equipment is shown in Fig. 1c. The tested substance is placed on a platform in the centre of the combustion chamber, 0.05 m above the floor. The platform was equipped with a load cell to determine the fuel mass loss. Experiments on the medium scale were performed under a variety of conditions using all the chemical substances with the exception of PP [6].

Gas analysis was performed on-line for CO_2, CO (non-dispersive IR-absorption), O_2 (paramagnetic), NO_x (chemiluminiscence) and content of unburned low molecular weight hydrocarbons, boiling point below 200°C, (flame ionisation detector). Grab samples were taken in the exhaust duct and were analysed with GC/MS with respect to high molecular weight components. The content of HCl and SO_2 were determined on samples taken intermittently from the exhaust duct. The analysis was made with ion chromatography.

The ϕ-value was measured with the ϕ-meter and for the experiments with only one opening these results were compared to values calculated with Eq. 5.

4.4 The ISO room set-up

The large-scale experiments [19], were performed inside a lightweight concrete room with dimensions in accordance with ISO 9705 [7], see Fig. 2d. The room had one opening: 0.8 m x 2 m. Changing the height of the opening altered the ventilation conditions. Heights of 0.9 m, 0.7 m, 0.6 m and 0.5 m were used during the experiments. GER values were determined with the ϕ-meter and ranged between 0.2 and 2.5. The fuel was put in pans of different sizes (0.5 m^2-1.4 m^2), the aim of which was to obtain about the same total heat release rate, irrespective of the substance being combusted. In these experiments, gas analysis was performed on-line on gas samples taken from the opening of the room, unburned hydrocarbons (flame ionisation detector), NO_x (chemiluminiscence), O_2 (paramagnetic) and H_2O, CO_2, CO, HCl, SO_2, HCN and NH_3 (FTIR). Grab samples were taken the combustion gases leaving the room and were analysed with GC/MS with respect to high molecular weight components. On-line measurements were also made on samples from the exhaust duct, unburned hydrocarbons (flame ionisation detector), NO_x (chemiluminiscence), CO_2 and CO (IR-absorption). Experiments were performed with all the substances mentioned above.

4.5 Analytical procedures

Characterisation and quantitative analysis of the components in the combustion gases were essential parts of the project. In order to facilitate comparison between experiments on different scales considerable effort was made to co-ordinate the measurements. On-line and off-line measurements were made on all scales to quantify a number of combustion gases such as O_2, CO, CO_2, NO_x, HCl, HCN and SO_2. In the DIN furnace and the cone calorimeter the on-line analysis was made with FTIR and in the medium-scale room analysis was with conventional techniques such as IR-spectroscopy and chemiluminiscence. In the ISO room conventional techniques were used for measurements in the exhaust duct and FTIR was used for analysis of samples taken in the opening of the room. The FTIR analysis in the cone calorimeter and the ISO room set-ups were made on filtered samples. In the con calorimeter the filter was heated to 130°C and in the ISO room the filter and the sampling lines were heated to 180°C and 200°C respectively. This means that particles and compounds adsorbed on the particles were not introduced into the FTIR analyser. In the DIN furnace experiments the sample passed glass wool before introduction to the FTIR instrument. The content of unburned hydrocarbons was also analysed on-line in the medium-scale room and in the ISO room. These on-line gas measurements gave continuous data on the concentration of the low molecular weight combustion products, with boiling points below 200°C.

Grab samples were taken from the combustion products in order to qualitatively and quantitatively analyse high-molecular-weight compounds in all set-ups. The samples were analysed with gas chromatography and/or mass spectrometry techniques. The samples were collected on adsorbing substrates, for example, XAD-2, Tenax or active carbon. The samples from the ISO room were led through a heated filter prior to the adsorption on the different substrates. In the DIN furnace experiments the sample was collected in a freezing trap, which was connected, to the GC/MS apparatus. In the other set-ups the samples were adsorbed directly onto the different substrates. More thorough descriptions of the methods used in the different scales are given in [6, 18,19,20] These methods of analysis give the cumulated production of the components analysed over the whole sampling period.

One important purpose of the GC/MS analyses was to determine what is here referred to as the “survival fraction”, which means the amount of the original substance that survives combustion. In addition to the gas measurements, the mass loss rate was also determined in all experiments. Measurements were made of smoke density and the rate of heat release too except in the DIN furnace experiments. In experiments with chlorine-containing substances, (CB and CNBA), the dioxin content in the combustion gases was analysed in the DIN furnace, the cone calorimeter set-up and in the ISO room set-up. These results are presented elsewhere [21].

5. Results and discussion

Results from the TOXFIRE experiments are presented below together with attempts to explain some of the findings. Results are presented from measurements of CO, CO_2, unburned hydrocarbons, survival fractions, HCl, HCN, NO_x and SO_2.

The production of combustion gases is presented as yields. The yield of a specific component is given as the ratio between the mass of the gas component produced, and the mass loss of the burned substance.

5.1 CO, CO_2 and unburned hydrocarbons

Many attempts have been made to correlate measurements of combustion gas concentrations in the fire plume with those in the upper layer with GER [22, 23]. Pitts [24] introduced an engineering approach for estimating carbon monoxide formation in enclosed fires. The major conclusions of earlier studies can be summarised as follows:

- Major flame species including CO can be correlated in terms of GER.
- The generation of CO, soot and unburned hydrocarbons under fuel-rich

conditions is considerably greater, and of CO_2 considerably lower, than under lean fuel conditions.

- Different mechanisms can affect reaction rates, i.e., for CO production quenching of a turbulent fire plume upon entering a fuel-rich upper layer, mixing of oxygen directly into a fuel-rich, high-temperature upper layer with subsequent reaction, pyrolysis in a high temperature and oxygen-vitiated environment or approach to full equilibrium combustion product concentrations in a fuel-rich, high-temperature upper layer.

Since the GER was used to compare the production of combustion gases in the different experimental set-ups it was important to find a representative way of determining the GER. In the medium-scale and in the ISO room, an equipment referred to as the ϕ-meter was used. In order to verify the function of the ϕ-meter results from calculations with Eq. 5 was used in the medium scale experiments where it was feasible. In Fig. 2, a comparison between measured and calculated ϕ-values is presented for an experiment with TMTM, Fig. 2a and for heptane, Fig. 2b. The experiment with TMTM was performed under well-ventilated conditions whereas the heptane experiment reached a ϕ up to almost 2. As can be seen in Fig. 2, the results are in good agreement for both types of situations.

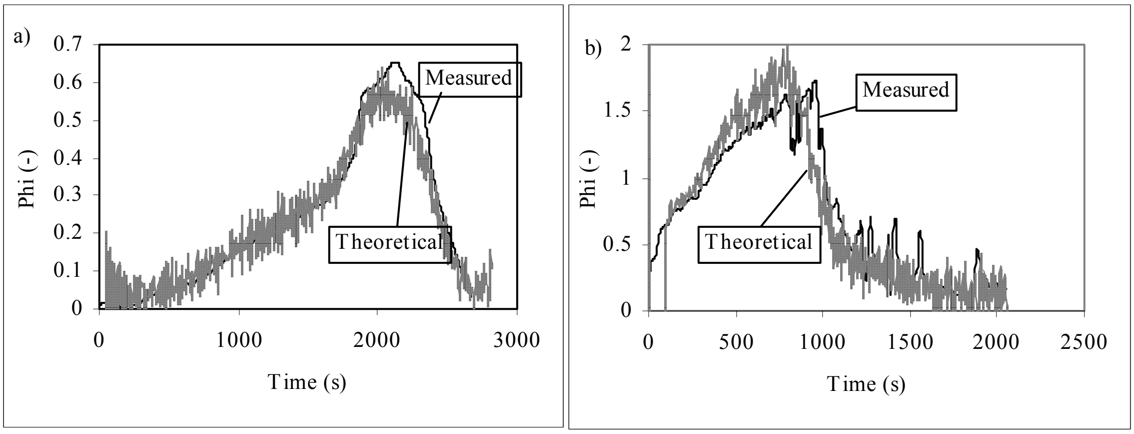


Figure 2. A comparison between measured and calculated ϕ-values for an experiment with a) TMTM in the 1/3 scale ISO room and b) for heptane in the 1/3 scale ISO room.

Recently, Tolocka et al. [25] showed experimentally that the yields of combustion gases are dependent on GER and temperature. They presented experimental results and the dependence of GER on combustion products confirming former results [22], that CO increases with GER, and that CO_2 increases with GER up to GER=1 and then decreases. They also found a pronounced temperature dependence indicating that GER is not the only parameter that can be used as a scaling factor. In the present study the GER was chosen as the reference parameter since it was readily available from experiments on all scales. In the experiments with organic fuels containing heteroatoms observations regarding the dependence of yields of CO_2 and CO on the GER were similar to those reported earlier. This is illustrated by the results presented in Fig. 3a where the ratio between the CO_2 yields and the maximum CO_2 yields for experiments with nylon on three different scales are shown as a function of the GER.

In experiments with chlorine-containing substances this relation was much weaker, as can be seen for CNBA in Fig. 3b. The yield of CO for PP is given in Fig. 4a as a function of the GER, and in Fig. 4b the CO yield versus GER is presented for CB. For PP there is a strong dependence between the GER and the yield of CO, but this is not as evident for CB. An explanation of this could be that chlorine-containing substances produce less heat during combustion showing low combustion efficiency. Because of this, chlorine has been much used for fire retardant purposes. During the experiments with CB in the ISO room some difficulties were encountered with the GER measurements [19]. This might explain why the data in Fig. 4b from the ISO room are not in line with the data from the other experiments.

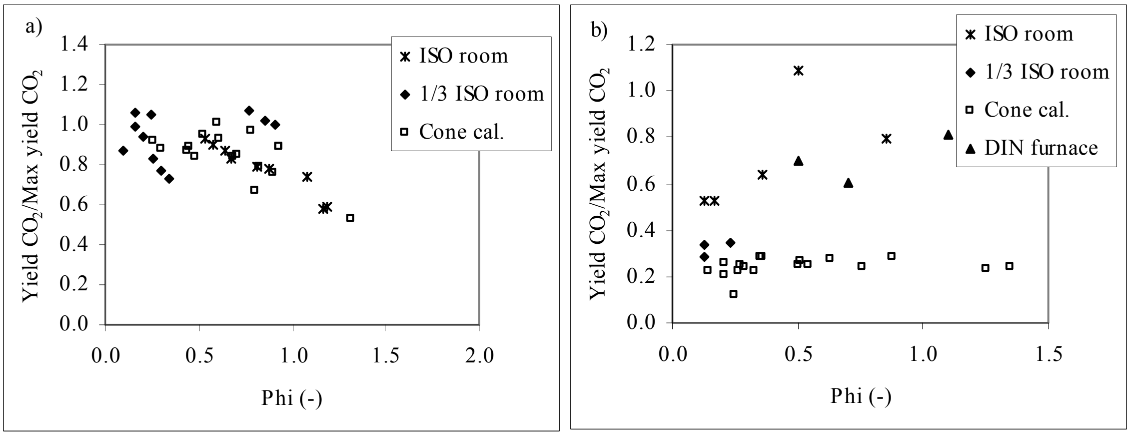


Figure 3 a) The ratio between the yield of CO_2 and the maximum theoretical yield (2.06 kg/kg [23]), as a function of the ϕ-value for experiments with nylon performed in the ISO room, the 1/3 ISO room, and in the cone calorimeter. b) The ratio between the yield of CO_2 and the maximum theoretical yield (1.27 kg/kg, calculated value), as a function of the ϕ-value for experiments with CNBA performed in the ISO room, the 1/3 ISO room, the cone calorimeter and the DIN furnace.

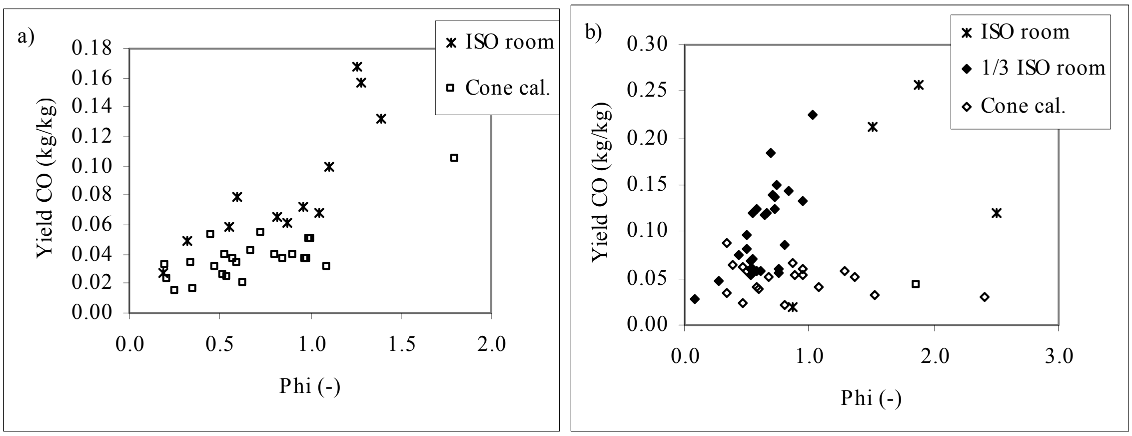


Figure 4 a) The yield of CO for experiments with PP as a function of the ϕ-value for experiments in the ISO room and the cone calorimeter. b) The yield of CO for experiments with CB as a function of the ϕ-value for experiments in the ISO room, the 1/3 ISO room and the cone calorimeter.

For the substances PP and nylon without chlorine the production of low-molecular-weight unburned hydrocarbons follows the expected pattern. As can be seen in Fig. 5a the yields of unburned hydrocarbons increase as the degree of ventilation decreases. When chlorine is present the results are quite different, see Fig. 5b and 5c. This could be due to the fact that the method of analysis, a flame ionisation detector, is unsuitable for measuring components containing heteroatoms, but it is also possible that more heavy components are produced and they cannot be detected with this method. The latter suggestion is supported by the amounts of original compound found after combustion.

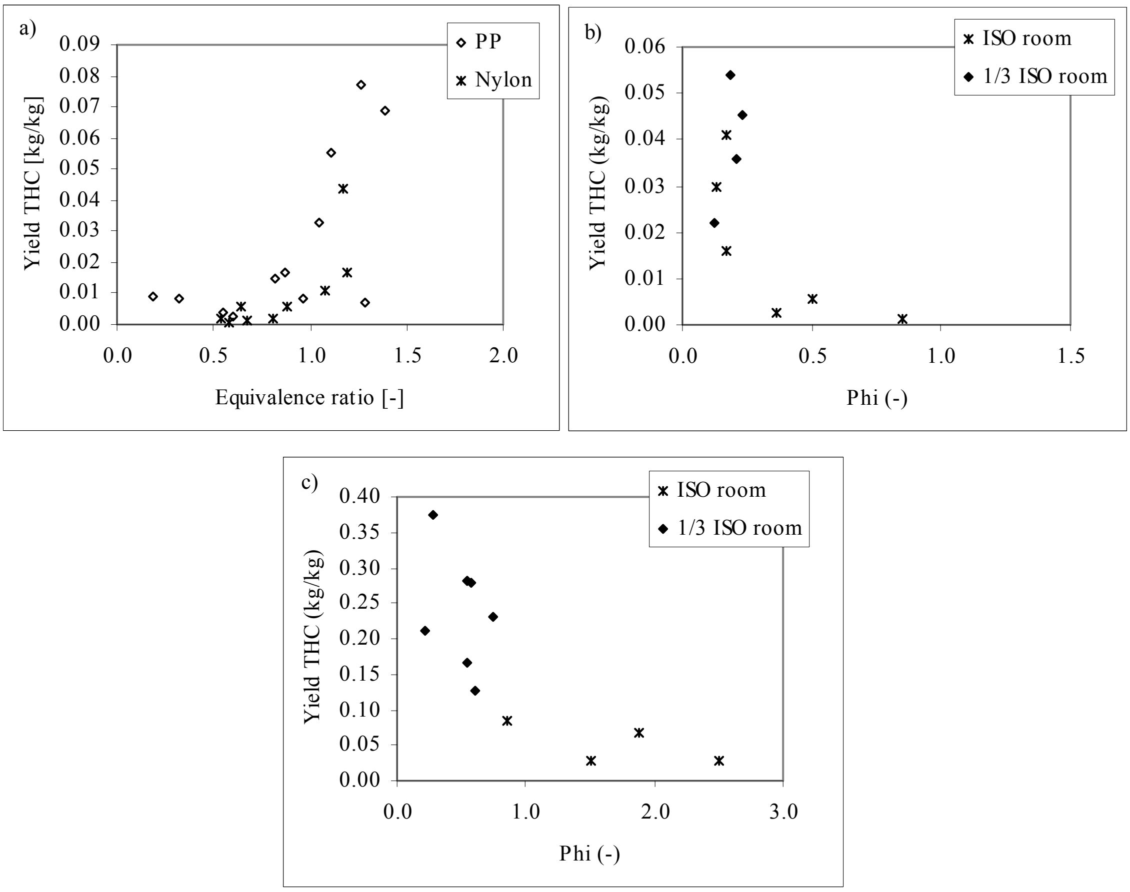


Figure 5 a) The yield of low-molecular-weight hydrocarbons from experiments with PP and nylon as a function of the ϕ-value for experiments in the ISO room. b) The yield of low-molecular-weight hydrocarbons from experiments with CNBA as a function of the ϕ-value for experiments in the ISO room and the 1/3 ISO room. c) The yield of low-molecular-weight hydrocarbons from experiments with CB as a function of the ϕ-value for experiments in the ISO room and the 1/3 ISO room.

5.2 Survival fraction

The survival fraction is the amount of the original compound in the combustion gases that is not burned and thus escapes in the fire plume. The yields are dependent on the physical and chemical properties of the burned compound and the combustion conditions. In the experiments presented here, measurable survival fractions were detected in the tests with CB and CNBA. These survival fractions are given in Table 2. The experiments with CB gave very large amounts of unburned compound. To be able to predict survival fractions of other compounds, their possible precursors must be examined. This is particularly important for toxic compounds, such as pesticides.

Table 2. Survival fraction of the original substance, after combustion, given in %.

Substance	ISO room	1/3 ISO room	Cone calorimeter
CB	2 - 5	3	4-8
CNBA	n.d.$^{1)}$	(<<2.8)$^{2)}$	0.2-0.3

$^{1)}$ CNBA was mixed with polypropylene in most experiments to improve the combustion

$^{2)}$ The yield is the amount of the THC, substantial amounts of other organic substances like chlorobenzene have been detected, and thus the amount of CNBA is much less than this.

The survival fraction may be considered as a measure of the stability of a compound during gasification and combustion. This means that under gasification a compound is stable when the onset temperature for its degradation is far from its melting and boiling points. At least the rate of degradation in the solid or liquid phase should be much slower than the rate of evaporation into the gas phase. This is often not the case for large molecules, especially polymers that degrade into smaller molecules prior to gasification [26]. In the gas phase the compound will be pyrolysed in the core of the flame. This process is dependent on the physical and chemical properties of the compound and on the reaction temperature.

In Fig. 6 some examples of pyrolysis rates are shown for CB, benzene (C_6H_6), toluene (C_7H_8), methane (CH_4), and ethane (C_2H_6). Benzene and methane have the lowest reaction rates, while toluene and ethane are more reactive. CB has a higher reaction rate than benzene and methane, but substantially lower than the others in the figure. The first three molecules have higher bond energies than the others.

The next stage of combustion will be reactions between free radicals and the compound. Thus, the reaction rates of the main radicals; OH·, H·, HOO· and others important for the oxidisation process must be slow in relation to the residence time of the molecule to give high survival fractions. In Fig. 7 the rates of the pseudo-first-order reactions of OH· with a number of compounds are plotted. Again, CB has one of the lowest rates, comparable with methane and CO. The main mechanism for these reactions is H· abstraction by the OH· radical. In such reactions the bond energy is an important factor in determining the reaction rate. And it will be similar for other free radicals. Thus compounds with no weak bonds may be expected to have high survival fractions, as they are less susceptible to thermal and oxidative degradation. It is evident that parameters, such as temperature and residence time will influence the final yields. Another important influence arises from compounds that react faster than CB with the available free radicals. These may be mixtures with other substances or low concentrations of pyrolysis products so that the combustion temperature is not increased. This will protect the compound from degradation. A similar situation is described in [27] for the oxidation process of CO to CO_2, which is inefficient as long as other organic substances are present in the flame. The reason is the low reaction rate of CO with OH· compared with the most common compounds in a flame.

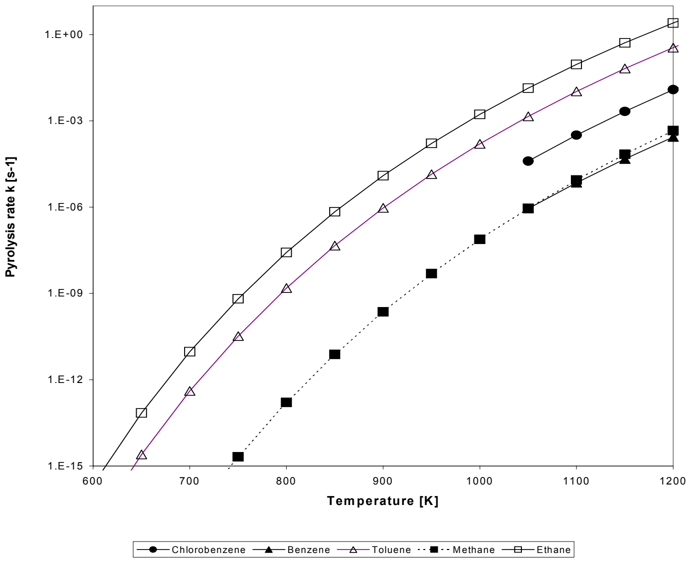


Figure 6. First-order pyrolysis rate data for some selected hydrocarbons. References for the pyrolysis rate data: Chlorobenzene [28,29],benzene [29], toluene [30], methane and ethane [31].

Under fuel-rich conditions methane and benzene may also be generated by the chemical reactions in the gas phase to some minor extent. Excluded from the above are heterogeneous reactions, e.g. reactions of adsorbed molecules on the surface of soot. The reactions with the free radicals can follow other pathways, which might enhance the reactivity of less reactive molecules present in the gas phase. One reason for this may be catalytic effects.

In experiments with the pesticide dichlobenil (2,6 dichloro-benzonitrile) in the cone calorimeter, survival fractions of 8-18% were reported by Hietaniemi et al. [18]. This substance is an aromatic chlorinated compound with the ability to stabilise the radicals and slow down the reaction rate, and therefore supports the discussion above concerning influences leading to high survival fractions.

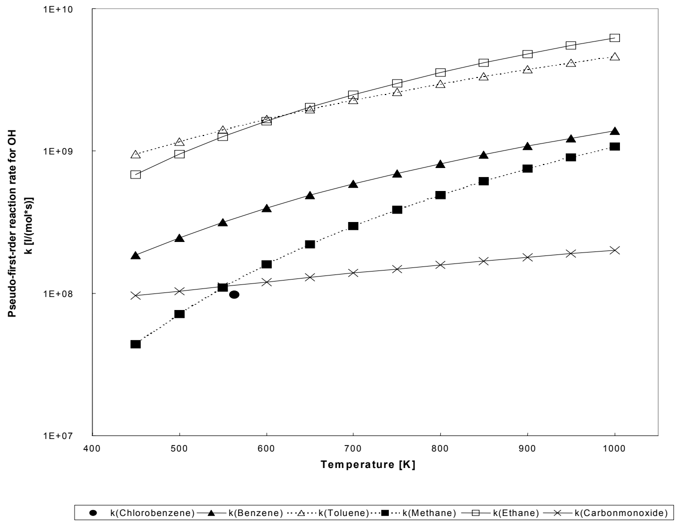


Figure 7. Reaction rates for the OH radical for some selected compounds in the temperature interval from 450 to 1000 K. References for the reaction rates: Chlorobenzene[32, 33], benzene [34], toluene [34], methane [35], ethane [36] and carbonmonoxide [39].

5.3 Hydrogen chloride

CNBA and CB contain chlorine and will give hydrogen chloride as a combustion product. The formation of this product as a function of the ϕ-value is shown for CNBA and CB in Fig. 8. The HCl yield seems to be largely independent of the ϕ-value for both substances, and about 50% of the theoretical maximum yield (dashed lines) was recovered. The HCl yield from CNBA measured in the DIN furnace was slightly more than 100%. A possible explanation of this is given by Markert [37]. During the tests with CNBA large amounts of soot were produced and the filters were blocked, giving a false measurement of the air flow through the tube. The true amounts of HCl produced are thus lower than the measured ones plotted in Fig. 8a.

For CNBA the DIN furnace had the highest CO_2 yields and for CB the highest values were obtained in the ISO room and in the 1/3 ISO room. Thus, it appears that the amount of heat produced during combustion is an important parameter in the generation of HCl. This is in agreement with the assumption that HCl is produced in the pyrolytic region of the flame, with the dissociation of the carbon-chlorine bond as the rate-limiting step. The latter is exponentially dependent on (flame) temperature, which increases with the amount of combustion heat produced. This is supported by additional DIN furnace experiments on CB at 500°C and 700°C where almost no HCl was formed [20]. A temperature of 900°C is needed to give high HCl yields of about 50% of the maximum yield. This high temperature is reasonable, as the dissociation energy for the carbon chlorine bond in CB is very high. The C-Cl bond dissociation energy in PVC, for example, is much lower and HCl is already formed above 200°C [38]. The DIN furnace experiments at 500, 700 and 900°C showed no dependence on temperature of the HCl yields [20].

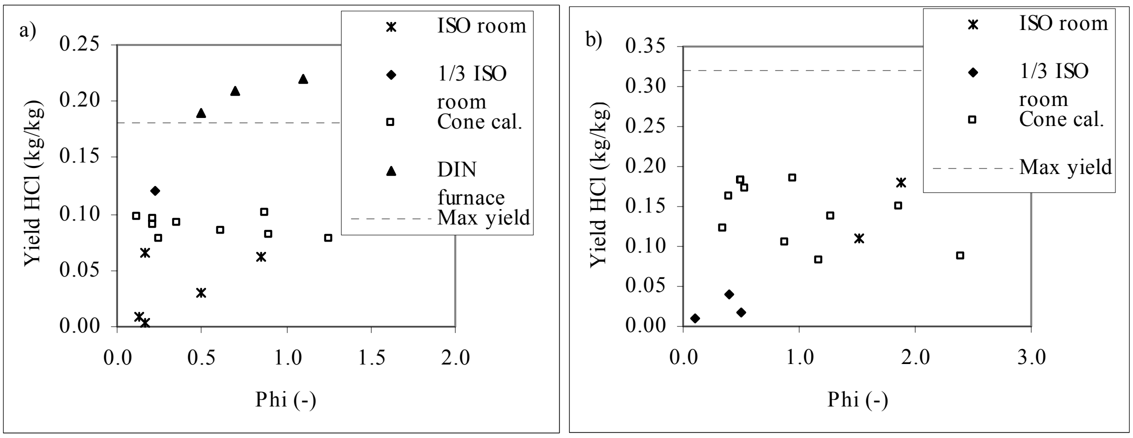


Figure 8 a) The yield of HCl from experiments with CNBA as a function of the ϕ-value for experiments in the ISO room, the 1/3 scale room, the cone calorimeter and the DIN furnace. b) The yield of HCl from experiments with CB as a function of the ϕ-value for experiments in the ISO room, the 1/3 ISO room and the cone calorimeter.

5.4 Hydrogen cyanide

Hydrogen cyanide (HCN) was formed in the experiments with CNBA, TMTM and nylon. These substances all contain nitrogen. The HCN yields as a function of the ϕ-value are presented in Fig. 9. In all cases the yields are rather low, with a maximum yield of around 4%. The HCN yields for CNBA measured in the cone calorimeter, the ISO room and the DIN furnace are in good agreement. In the case of TMTM and nylon some scatter in the yields can be observed. For TMTM and nylon an increase in HCN yield with increasing ϕ-value can be seen. This is to be expected, while it was not observed for CNBA. The HCN yields are consistent between the test methods and they are relatively constant over the range of ϕ investigated. CNBA is a chlorine-containing substance and this could contribute to the difference in its behaviour compared with the compounds without chlorine. This difference might also be explained by additional parameters influencing the HCN yield, such as the (flame) temperature. This is reasonable as HCN formation and consumption in a flame are very complex, involving both pyrolytic and oxidation reactions, which depend on temperature and on both temperature and ϕ-value, respectively. This can be seen from the TMTM results obtained in the DIN furnace [37]. Here, three measurements were made at different ϕ-values at 500°C and three at 900°C. All the upper values correspond to the 500°C measurements, thus indicating a higher HCN yield at a lower temperature under otherwise identical flow conditions. HCN was not analysed in the 1/3 ISO room studies.

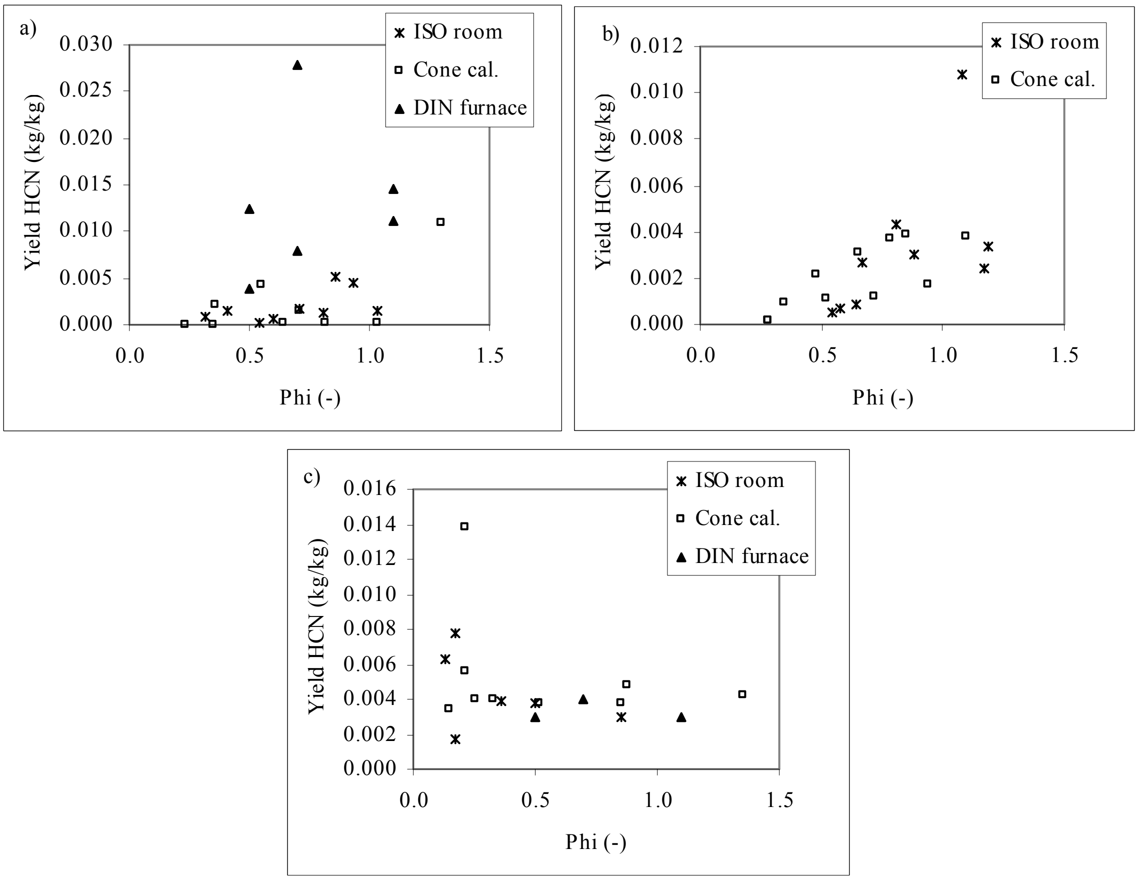


Figure 9 a) The yield of HCN from experiments with TMTM as a function of the ϕ-value for experiments in the ISO room, the cone calorimeter and the DIN furnace. b) The yield of HCN from experiments with Nylon as a function of the ϕ-value for experiments in the ISO room and the cone calorimeter. c) The yield of HCN from experiments with CNBA as a function of the ϕ-value for experiments in the ISO room, the cone calorimeter and the DIN furnace.

5.5 Nitrogen oxides (NO_x)

CNBA, TMTM and nylon, which all form hydrogen cyanide, will also form nitrogen oxides. The sum of the NO and NO_2 emissions (NO_x) are compared in Fig. 10a, b and c for the different scales. It can be seen from the plots that CNBA, TMTM and nylon give roughly the same yields of NO_x, all increasing with lower ϕ-values. This is also the behaviour described in the literature [39, 40]. It can be concluded that the results from the experiments on the four scales are in good agreement.

The NO_x may also be formed by reactions with the nitrogen in the air by two main reactions giving “thermal or Zeldovich NO” and “prompt or Fenimore NO” [39]. The former is favoured at very high flame temperatures, which are less likely during uncontrolled combustion, especially for CNBA, which burned rather poorly. Prompt NO formation is due to the reaction of free CH radicals with N_2 at the flame front. This may have given a minor contribution to the overall NO_x yields found in these experiments. Nevertheless, these contributions are expected to be small and the major part of the NO_x emissions will be due to the nitrogen in the fuel.

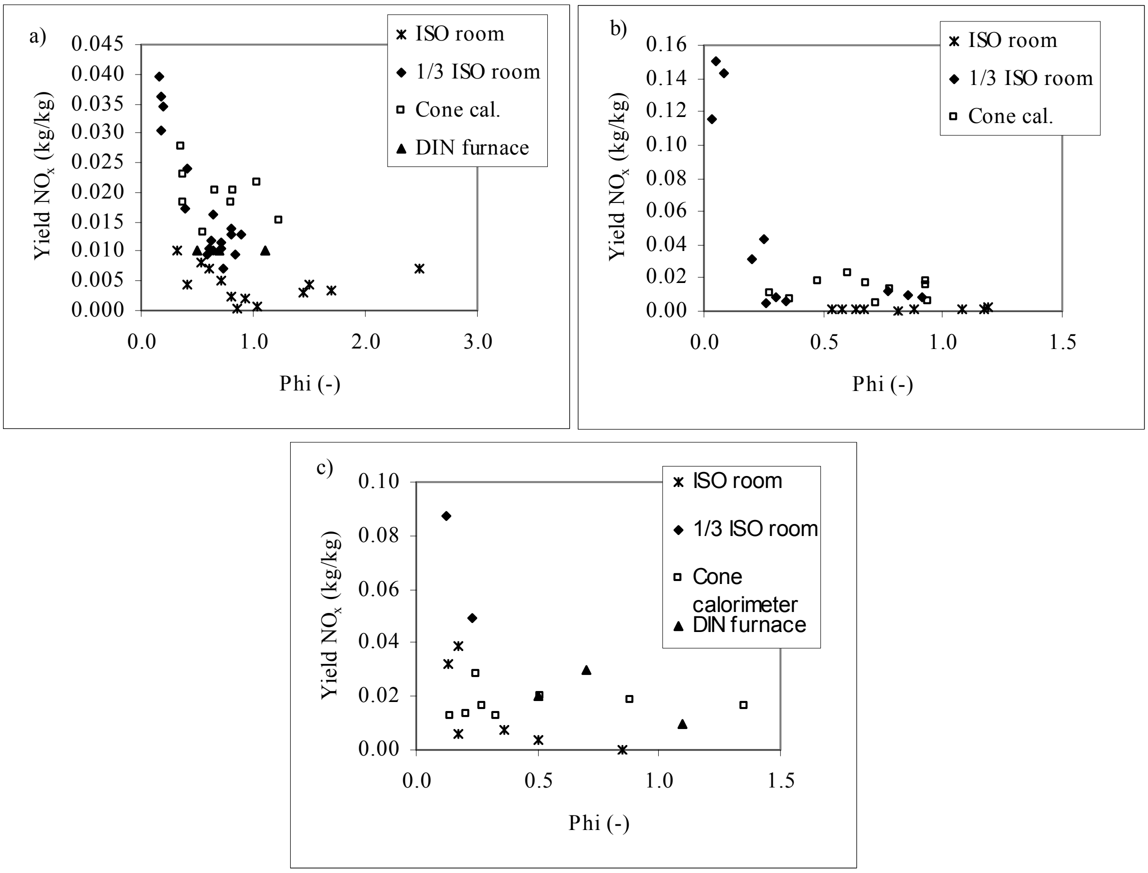


Figure 10 a) The yield of NO_x from experiments with TMTM as a function of the ϕ-value for experiments in the ISO room, the 1/3 ISO room, the cone calorimeter and the DIN furnace. b) The yield of NO_x from experiments with Nylon as a function of the ϕ-value for experiments in the ISO room, the 1/3 ISO room and the cone calorimeter. c) The yield of NO_x from experiments with CNBA as a function of the ϕ-value for experiments in the ISO room, the 1/3 ISO room, the cone calorimeter and the DIN furnace.

Comparing the three substances shows that they all give similar yields. This is remarkable as CNBA has only one nitrogen atom per molecule, whereas TMTM and nylon contain two nitrogen atoms in their molecules or repeating units, and they have approximately the same molecular weights, 201.6, 208.4 and 226.4 g/mol, respectively. It is expected that prompt NO formation would be small compared with the overall NO_x formation. CNBA contains a NO_2-group attached to the aromatic ring. NO_x might therefore be directly released from the molecule during combustion in a pyrolytic reaction [41]. For TMTM and nylon the nitrogen will therefore follow the normal fuel-nitrogen conversion mechanism [39], where the final NO_x is formed via oxidation of initially formed hydrogen cyanide.

5.6 Sulphur dioxide

TMTM was the only sulphur-containing substance included in the experiments. The SO_2 content of the combustion gases was analysed in three cases, the DIN furnace, the cone calorimeter and the ISO room. The SO_2 yields obtained in these set-ups are presented in Fig. 11. It was found that the sulphur dioxide yield was about 100% at ϕ-values smaller than 1, and decreased for ϕ-values greater than 1. This is in agreement with the expected results. The DIN furnace results are somewhat below the results for the cone calorimeter and the ISO room. The three highest points of the six data points resulting from the DIN furnace experiments are from the 900°C experiments and the three lower points correspond to combustion at 500°C. Thus, a lower SO_2 yield was found at the lower temperature, which is as expected. Also, the results from the DIN furnace at 900°C are a lower limit only, as the calibration limits were exceeded during the combustion experiments.

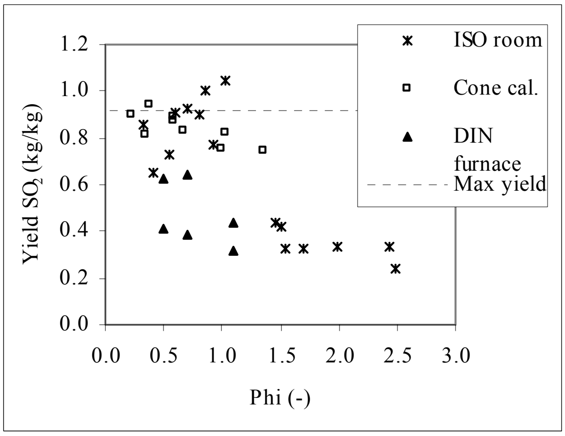


Figure 11. The yield of SO_2 from experiments with TMTM as a function of the ϕ-value for experiments in the ISO room, the cone calorimeter and the DIN furnace.

6. Conclusions and final remarks

The influence of scaling on the type and quantity of combustion gases resulting from fires involving chemicals containing heteroatoms has been studied. The experiments were conducted in order to find methods of assessing the consequences of warehouse fires involving chemicals. The tests were performed within the TOXFIRE project [2], which provided extended knowledge on the fire products for a number of chemicals under different combustion conditions. The results of scaling with four products containing heteroatoms, (CNBA, TMTM, nylon, CB) and one substance containing carbon and hydrogen (PP) are presented.

The yields of hydrogen chloride and sulphur dioxide are high compared with the maximum theoretical yields, which is in agreement with the assumption that these compounds are “end products” in the case of well-ventilated fires. Hydrogen chloride will also be generated under pure pyrolytic conditions and can thus be an important combustion gas, even under poorly ventilated conditions. During the tests, the amounts of unburned compounds in the combustion gases, the survival fraction, was determined for CB and CNBA. For CB survival fractions as high as 3 to 8% were measured.

The overall scaling results were found to be in good agreement for the qualitative analysis of the combustion gases and satisfactory regarding the quantitative results, as the results are within one order of magnitude or better. This shows that experiments on all the scales tested can be used to predict the consequences of a fire involving chemicals.

References

1 Markert, F., “Assessment and mitigation of consequences of fires in chemical warehouses”, Safety Science 30 (1998), 33-44.

2 Petersen, K.E., Markert, F., ”Assessment of Fires in Chemical Warehouses. An overview of the TOXFIRE project”. Risø-R-932 (EN). Risø National Laboratory, Roskilde. December 1996.

3 Fardell, P. J., Woolley, W. D., ”State of the art of combustion toxicity”. International Conference: Fire: Control the Heat. Reduce the Hazard. 24-25 October 1988, London, UK. Organised by QMC Fire & Materials Centre, 12.1-12.12.

4 Deutsche Normen, 1981, DIN 53436. ”Erzeugung thermischer Zersetzungsprodukte von Werkstoffen unter Luftzufuhr und ihre toxikologische Prüfung”, Teil 1, 2, 3.

5 ISO 5660-1 (1993). “Fire tests – Reaction to fire – Rate of heat release from building products – Cone calorimeter method”.

6 Andersson, B., Babrauskas, V., Holmstedt, G. Särdqvist, S., Winter, G., ”Simulated fires in substances of pesticide type”. Department of Fire Safety Engineering, Lund University, Report 3087, 1996.

7 ISO 9705:1993(E), “Fire tests – Full-scale room test for surface products”.

8 Babrauskas, V., Parker, W. J., Mulholland, G., Twilley, W. H., ”The phi meter: A simple, fuel-independent instrument for monitoring combustion equivalence ratio”, Rev. Sci. Instrum. 65(7), July 1994, 2367-2375

9 Babrauskas, V., “Fire Endurance in Buildings”, Report No UCB FRG 76-16, November 1976, Fire Research Group, University of California, Berkeley, USA.

10 Thomas, P. H., Heselden, A. J. M. and Law, M., ”Fully-developed compartment fires – two kinds of behaviour”, Fire Research Technical Paper No. 18, 1967.

11 Kawagoe, K., “Fire Behaviour in Rooms”, Report of the Building Research Institute, No. 27, 1958.

12 Steckler, K., D., Quintiere, J., G., Rinkinen,, W., J., “Flow Induced by Fire in a Compartment“, Nineteenth Symposium (International)/The Combustion Institute, 1982, 913-920.

13 Prahl, J. And Emmons, H. W., “Fire Induced Flow through an opening”, Division of Engineering and Applied Physics, Harvard University, Cambridge Massachusetts, USA, Technical report No. 12, 1975.

14 Markert, F., ”Micro scale experiments to assess combustion gases generated in chemical fires” 3rd Seminar on European research on industrial fires, 17-18 Sep. 1996, Risø National Laboratory, Roskilde, Denmark, 55-63.

15 ISO/TR 9122-1 (1989). ”Toxicity testing of fire effluents ”- Part 1: General.

16 ISO/TR 9122-4 (1993) ”Toxicity testing of fire effluents ”- Part 4: The fire model.

17 Mikkola, E., “Effects of Oxygen on Cone Calorimeter Results”. Interflam ´93. 6th International Fire Conference, Oxford, UK, 30 March – 1 April 1993. Carole A.. Franks (ed.). Interscience Communications Ltd., 49 – 56.

18 Hietaniemi, J., Kallonen, R., Mikkola, E. ”Fires at chemical warehouses. A cone calorimeter study on the burning characteristics and fire effluent composition of selected chemical compounds”. VTT Research Notes 1810, 1997.

19 Lönnermark, A., Blomqvist, P., Månsson, M., Persson, H. “TOXFIRE – Fire Characteristics and Smoke Gas Analysis in Under-Ventilated large-scale Combustion Experiments. Tests in the ISO 9705 Room.” SP Report 1996:45, Borås, Sweden, 1997.

20 Smith-Hansen, L., Jørgensen, K. H-, ”Combustion of Chemical Substances and the Impact on the Environment of the Fire Products – Microscale Experiments” Risø-R-651 (EN), 1992, Risø National Laboratory, Roskilde, Denmark.

21 Vikelsø, J., Johansen, E., ”Estimation of dioxin emission from fires in chemicals”, Chemosphere 40 (2000), 165-175.

22 Pitts, W. M., “The global equivalence ratio concept and the formation mechanisms of carbon monoxide in enclosure fires”, Prog. Energy Combust. Sci. 21 (1995), 197 – 237.

23 Tewarson,A., "Generation of heat and chemical compounds in Fires", SFPE handbook 2nd ed. 1995, Section 3/Chapter 4.

24 Pitts, W.M. "An Algorithm for Estimating Carbon Monoxide Formation in Enclosure Fires." Proceedings of the 5th International Symposium of The international Association for Fire Safety Science, Melbourne Australia, 3-7 March 1997, 535-546.

25 Tolocka, M.P., Richardson, P. B. and Houston Miller, J., "The Effect of Global Equivalence Ratio and Postflame Temperature on the Composition of Emissions from Laminar Ethylene/Air Diffusion Flames" Combustion and flame, (1999), 118:521–536.

26 Drysdale, D., "An Introduction to Dire Dynamics", John Wiley and Sons, 1985, ISBN 0-471-90613-1.

27 Pitts, W. M., "Application of Thermodynamic and Detailed Chemical Kinetic Modeling to Understanding Combustion Product Generation in Enclosure Fires", Fire Safety Journal 23 (1994), 271-303.

28 Ritter, E. R. And Bozzelli, J. W., "Kinetic study on thermal decomposition of chlorobenzene diluted in H_2", J. Phys. Chem. 94 (1990), 2493-2504.

29 Rao, V. S. and Skinner, G. B., "Formation of H and D atoms in pyrolysis of Benzene-d_6, chlorobenzene, bromobenzene and iodobenzene behind shock waves", J. Phys. Chem., 92 (1988), 2442-2448.

30 Brand, U., Hippler, H., Lindemann, L. And Troe, J., " C-C and C-H bond splits of laser-excited aromatic molecules. 1. Specific and thermally averaged rate constants", J. Phys. Chem., 94 (1990), 6305-6316.

31 Tsang, W. and Hampson, R. F., "Chemical kinetic data base for combustion chemistry. Part I. Methane and related compounds", J. Phys. Chem. Ref. Data., 15 (1986), 1087-1279.

32 Mulder, P., "Autooxidation of chlorobenzene between 500 – 1100 K", J. Chem. Soc. Perkin Trans 2, 1986, 1541.

33 Mulder, P. and Louw, R., "Kinetic H/D isotope effects for gas phase hydroxylation of benzene and chlorobenzene between 520 and 1080K", Int. J. Chem. Kinet. 20 (1988), 577.

34 Atkinson, R., "Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions", Chem Rev. 86 (1986), 69-201.

35 Baulch. et. al., J. Phys. Chem. Ref. Data., 15 (1986), 465.

36 Cohen, N. and Westberg, K. R. "Chemical kinetic data sheets for high-temperature chemical reactions", J. Phys. Chem. Ref. Data., 12(1983), 531-590.

37 Markert, F., "Results for CNBA and TMTM combustion in DIN furnace", Risö Report 883, Risö National Laboratory, Roskilde, Denmark, 1996.

38 Woolley, W. D. and Fardell, P.J., "Basic aspects of combustion toxicology". Fire Safety Journal 5 (1982), 29-48.

39 Warnatz, J. Maas, U. and Dibble, R. W., "Combustion", Springer Verlag 1996, ISBN 3-540-60730-7.

40 Cox (ed.) "Combustion Fundamentals of Fire", Academic Press 1995, ISBN 0-12-194230-9.

41 Buckley, Robinson, Baxter, "The reapplication of energetic materials as boiler fuels". Proceedings at The 5th Annual Global Demilitarisation Symposium, Reno NV, May 5-8, 1997.