Fire hazard analysis of hetero-organic fuels - Source characteristics from experiments

Andersson, Berit

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- Source characteristics from experiments

Berit Andersson

Department of Fire Safety Engineering
and Systems Safety

Lund University

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Berit Andersson

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Abstract
Source characteristics from experiments with hetero-organic fuels are presented. The results are intended as input to fire hazard analysis. The results imply that it is possible to use experiments in reduced scale to get an indication of the combustion products that can be produced in a fire with hetero-organic fuels as well as the levels of yields that can expected in a fire involving chemicals.

Brandteknik
och riskhantering
Lunds tekniska högskola
Lunds universitet
Box 118
221 00 Lund

brand@brand.lth.se
http://www.brand.lth.se

Telefon: 046 - 222 73 60
Telefax: 046 - 222 46 12

Department of Fire Safety Engineering
and Systems Safety
Lund University
P.O. Box 118
SE-221 00 Lund
Sweden

brand@brand.lth.se
http://www.brand.lth.se/english

Telephone: +46 46 222 73 60
Fax: +46 46 222 46 12

Summary

Fires in general cause problems to society at large since they can pose a threat to humans, property and to the environment. When toxic substances are involved in the fire, the problem is even more serious since the smoke from such a fire contains combustion products many of which are highly toxic.

To prevent, or at least minimise the consequences of fires is a big challenge. One way of dealing with this is to perform fire hazard analyses. Such hazard analyses rely on good models and high-quality input data. This thesis is aimed at providing such data for one type of fires: namely fires where hetero-organic fuels are involved. These fuels are essentially hydrocarbons where elements such as nitrogen, sulphur, chlorine and fluorine are incorporated into the molecule. Data, given as source characteristics, from experiments involving such chemicals are presented.

Reproduction of a real fire or at least a close facsimile to a real fire demands large-scale-testing. This is costly and often impractical for many reasons. Therefore experiments at a reduced scale must be employed. Results from a number of test-scales are compared, and it was found that simple correlations for scaling of important parameters such as yields of combustion gases do not apply for fuels with hetero-atoms.

Extinguishing agents were also incorporated into the study. They are not to be seen as fuels but they do represent organic hydrocarbons with hetero-atoms, mainly fluorine, that are intended to be applied on burning materials. It was found that when the application rate is below the extinguishing limit, large amounts of undesirable combustion products such as HF and COF_2 are produced. The same applies if the application of the extinguishing media is made too late and the fire has been allowed to grow.

It is common practice to present data from fire experiments as depending on the ventilation conditions during the experiment. These types of data are presented in the thesis but it was also found that other types of dependencies such as temperature and residence time are important. This is especially true for the substances containing hetero-atoms.

The overall results imply that it is possible to use small-scale experiments to get an indication of the combustion products that can be produced in a fire with hetero-organic fuels as well as the levels of yields that can expected in a fire involving chemicals.

Sammanfattning

Bränder orsakar generellt skador på människor, egendom och miljö och bränder som involverar giftiga kemikalier som kan ge förbränningsprodukter med innehåll av toxiska föreningar orsakar än större problem för samhället.

Att försöka förhindra eller i varje fall minimera skador från bränder är en stor utmaning. Ett sätt att tackla detta är att genomföra brandriskanalyser. Dessa analyser kräver bra beräkningsmodeller och data av hög kvalité som input till modellerna. Denna avhandling har som mål att ta fram input för en typ av bränder nämligen: bränder där bränslen innehållande hetero-atomer ingår. Denna typ av bränslen är huvudsakligen kolväten som i sin struktur även innehåller kväve, svavel, klor eller fluor. Resultat, i form av källtermer, från försök med denna typ av kemiska föreningar presenteras.

Att återskapa en verklig brand eller i varje fall något som liknar en verklig brand kräver genomförande av försök i näst intill verklig skala. Detta är kostsamt och opraktiskt av många skäl och därför genomförs försök oftast i mindre skala. I avhandlingen jämförs resultat från försök som har genomförts i olika stora skalor och resultaten visar att det är svårt att hitta enkla samband mellan dessa resultat när det gäller bränslen som innehåller hetero-atomer.

Försök med släckmedel har också genomförts. Dessa är inte att ses som bränslen men de representerar ämnen innehållande hetero-atomer, huvudsakligen fluor, och de är avsedda att användas mot brinnande föremål. Resultaten visar att om påföringshastigheten är under den mängd som behövs för att släcka branden så bildas oönskade förbränningsprodukter såsom HF och COF_2. Det samma gäller om släckmedlet sätts in alltför sent och branden har hunnit växa till utöver det inledande stadiet.

Det är vanligt att redovisa försöksresultat från brandförsök som beroende av ventilationsförhållandena under försöket. Denna typ av resultat redovisas även här men resultaten visar också att till exempel produktionen av förbränningsprodukter är beroende även av andra variabler. Dessa kan vara temperatur och uppehållstid i det varma gaslagret. Det har visat sig att denna typ av beroenden är särskilt påtagliga för föreningar som innehåller hetero-atomer.

Som en slutsats kan anföras att det är möjligt att använda småskaliga försök för att få en uppfattning om de förbränningsprodukter som kan bildas vid en brand med kemikalier innehållande hetero-atomer. Även storleken på produktionen av förbränningsprodukter vid kemikaliebränder kan uppskattas.

Preface

Fire has always been important to humans as a means of providing heat for keeping warm and in preparation of food, on the positive side. The fear of fire has therefore also been constantly present. Despite this, the research field of fire science is relatively new compared to other areas of natural sciences such as physics and chemistry. My first steps into the research area of fire science were in the late 1970's when the research was slowly changing from the fire resistance of structures into studies of the early stages of fires in enclosures. I took part in projects where the behaviour of upholstered furniture and beds was studied, as well as the behaviour of wall-lining materials in enclosures. These studies were aimed at obtaining data on flame spread, temperature in the enclosure and time to complete involvement of the enclosure flash over. Measurements of carbon monoxide and carbon dioxide were often made, as well.

As measurement methods for combustion products became more accessible and more adapted to measurements outside the chemical laboratory the possibilities to determine toxic combustion products from fire experiments became of interest. This made the studies carried out within the TOXFIRE project feasible. This project and a preceding EU project (STEP) were conducted during the 1990's and reflected well the shift of interest in the field of fire research.

Today, one focus of fire research, and primarily that concerning the production of combustion gases, is naturally influenced by the ongoing discussions related to climate change. Interest in fire hazard analysis, including life cycle analysis, has thus grown considerably.

This thesis is aimed at producing input to fire hazard analysis of organic fuels, especially those containing hetero-atoms such as N, Cl, S and F. My interest has always been to find answers to what happens in a fire by means of conducting experiments and to draw conclusions from experimental results.

My supervisor, Professor Göran Holmstedt, deserves special appreciation for pushing me to write the thesis and for valuable discussions on interesting topics within the area of fire science.

The supportive and stimulating atmosphere within the Department of Fire Safety Engineering and Safety Systems also made the work easier and more inspiring. A special thanks to Sven-Ingvar Granemark is appropriate for his help with instrumentation and solutions to those practical problems that always arise during experimental work.

Without the support of my family during many years of struggle towards the goal, I would never have succeeded. Thorbjörn, Katrin and Patrik, you helped me more than you will ever know.

Södra Sandby, 6 October 2009

Berit Andersson

Publications included in the thesis

Paper I

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

Berit Andersson, Frank Markert and Göran Holmstedt

Fire Safety Journal, Volume 40, Issue 5, 2005, 439-465.

Paper II

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, 295-308.

Paper III

Experimental study of thermal breakdown products from halogenated extinguishing agents

Berit Andersson and Per Blomqvist

Paper submitted to Fire Safety Journal.

Contributions in the appended papers

Paper I: I wrote most of the paper (90 %), conducted the medium-scale experiments, made the analysis and formulated the conclusions from the experimental results.

Paper II: I wrote the entire paper, conducted the experiments with the modified phi-meter, presented the results and formulated the conclusions. I also presented the paper at the seventh IAFSS symposium.

Paper III: I wrote most of the paper (75 %), planned the experimental setup and the test series. The experiments were conducted in cooperation with my co-author. I was responsible for all measurements except the FTIR, compiled the results and formulated the conclusions.

Publications not included in the thesis where the author has contributed

Scientific journals

I. *Fire behaviour of upholstered furniture – An experimental study*
Andersson, B. and Magnusson, S. E.
Fire and Materials, Vol. 9, No 1, 1985, pp 41-45

II. *Modelling of furniture experiments with zone models*
Blomqvist, J. and Andersson, B.
Fire and Materials, Vol. 9, No 2, 1985, pp 81-87

International conferences

III. *Fire behaviour of upholstered furniture – An experimental study*
Andersson, B. and Magnusson, S. E.
Presented at Interflam 82, University of Surrey, Guildford, March 30 – April 1, 1982

IV. *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

V. *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

VI. *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

VII. *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

VIII. *Scaling experiments to assess chemical warehouse fires*
Markert, F., Andersson, B. and Holmstedt, G.
Published at the SAFETYNET, Internet seminar, 1999

IX. *Effectiveness and thermal breakdown products of fire suppression agents*
Andersson, B., Holmstedt, G. and Blomqvist, P.
Poster presented at the Eighth IAFSS Symposium, Beijing, China, September 18-23, 2005, p 1602

Other publications

X. *Brand i stoppmöbler : en experimentell studie*
Andersson, B. and Magnusson, S. E.
Department of Structural Mechanics, Bulletin [19] 80:4, 1980

XI. *Fire behaviour of upholstered furniture : an experimental study*
Andersson, B. and Magnusson, S. E.
Division of Building Fire Safety and Technology, Report 3005, 1982

XII. *Fire behaviour of beds and upholstered furniture: an experimental study (second test series)*
Andersson, B.
Division of Building Fire Safety and Technology, Lund University, Report 3023, 1985

XIII. *Model scale compartment fire tests with wall lining materials*
Andersson, B.
Department of Fire Safety Engineering, Report 3041, 1988

XIV. *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

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

XVI. *Combustion products from fires – Influence from ventilation conditions*
Andersson, B.
Licentiate Thesis, Department of Fire Safety Engineering, Lund University, Report 1029, 2003

XVII. *Thermal breakdown of extinguishing agents*
Andersson, B., Blomqvist, P. and Dederichs A.
Department of Fire Safety Engineering and Systems Safety, Lund University, Report 3137, 2008

Contents

APPENDIX - PAPERS

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 around 100 every year, and about 1000 people require medical care due to fire-related injuries. The economic losses due to fire are of the order of SEK 5,700 millions per year [1].

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 thesis the focus is on combustion of materials, substances and extinguishing agents containing hetero atoms. Hetero atoms are defined as elements such as nitrogen, sulphur, chlorine and fluorine. When materials or substances containing these elements are exposed to fire they produce combustion products that can be highly toxic or harmful to humans, to the environment or to property.

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

The objective of this work is to give a general introduction to the production of combustion gases during fire with special emphasis on chemicals containing hetero-atoms such as nitrogen, sulphur, chlorine and fluorine. The results from two projects, the TOXFIRE project and a project dealing with halon replacement extinguishing agents will serve as reference for presented theories and results.

1.1.1 TOXFIRE

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 [2]. The fire took place in a warehouse where 1.25 million kg of 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 accumulated. 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 that is presented in this thesis 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 on 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 [3].

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-making system was developed for use by the Fire Chief in the event of a chemical fire. To achieve these objectives, the project was divided into a number of discrete work packages. An overview of the project is presented in Figure 1.

The project is summarised in the final report by Petersen and Markert [4], where a comprehensive list of publications emanating from the project is included. The work referred to in this thesis is restricted to the experimental part of the TOXFIRE project and referred to in Figure 1 as Source Characteristics [5, 6, 7, 8, 9]. The main contribution from Lund University in this part of the TOXFIRE project consists of medium-scale experiments [9].

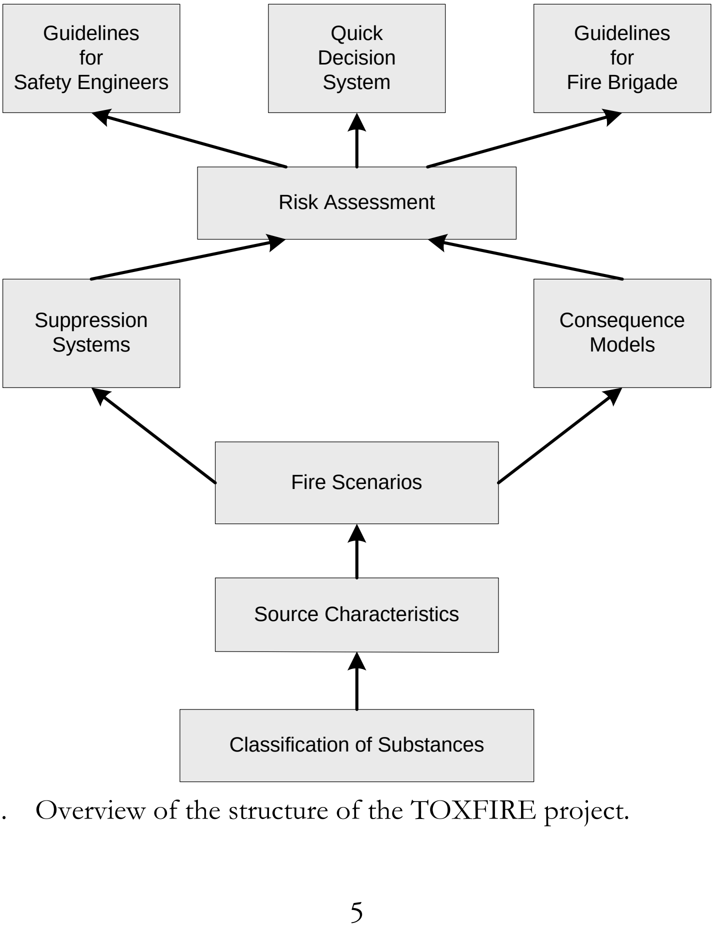


Figure 1. Overview of the structure of the TOXFIRE project.

1.1.2 Halon replacement agents

Until recently fluorinated, chlorinated and brominated hydrocarbons such as CF_3Br and CF_2ClBr were extensively used as fire suppression agents. Unfortunately halons have high stratospheric ozone depletion potential and can no longer be used. It is therefore vital to find new agents which have the same good fire-suppression qualities i.e. substances which are easy to produce, store and transport, are effective extinguishing agents which are not harmful to the humans who use them and are not damaging to the materials around the fire. This latter property is very important in aircrafts, computer systems and libraries, for example. Extensive research has been conducted on alternative agents that have these favourable properties while posing no risk of damaging the stratospheric ozone layer.

In order to control the use and to facilitate the phasing-out of ozone-depleting substances, international treaties have been designed and adopted. The Montreal Protocol was adopted in 1987 and entered into force in 1989. After that date, a number of amendments were made to the document. In 1997, yet another treaty to protect the ozone layer against greenhouse gases was adopted at Kyoto. This treaty entered into force in 2005. To further strengthen and clarify the text in the above mentioned protocols, the European Parliament has formulated additional regulations.

Different approaches have been used to find new systems for fire extinguishment, such as:

- Water mist

- Inert gases

- Aerosols and powders

- Halogenated liquids and pressure-condensed gases

Among these, the pressure condensed gases are those which have properties most similar to the halons. Many of these new agents contain fluorine (F) and can produce hydrogen fluoride (HF) and other fluorinated compounds when in contact with flames. HF is dangerous to humans [10] so this potential problem must be addressed before introducing new agents on the market.

A project funded by Brandforsk with supporting funding via the EU Large Scale Facility program and Solvay Fluor GmbH was initiated in order to investigate the potential of new chemical compounds as fire extinguishing agents [11]. The goal was to measure their extinguishing capability under different fire conditions as well as to analyse thermal breakdown products. This was in order to estimate possible application areas for the chemical compounds as halon replacement agents and to identify the effects of thermal breakdown products on humans, environment and materials. The project has both experimental and theoretical parts.

2 Fire scenarios

In order to study what happens during a fire and how different parameters influence the development of the fire it is necessary to find representative scenarios that can be employed in systematic studies of fire and fire conditions. In the two projects that are used here as examples a number of scenarios have been used ranging from micro-scale to large industrial scale. A presentation of these scenarios and the substances which were studied follows.

2.1 TOXFIRE

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.

2.1.1 Micro-scale experiments

Micro-scale combustion experiments were conducted in a DIN 53436 furnace The DIN furnace set-up is presented in Figure 2 [5]. The set-up was composed of a quartz tube with the dimensions: length 1 m and diameter 4 cm and a movable annular electric oven which enclosed a section of the tube. The oven moved at a velocity of 0.01 m/min. The sample, weighing 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 the combustion products were led 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. These 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 and the results are presented in [5, 6].

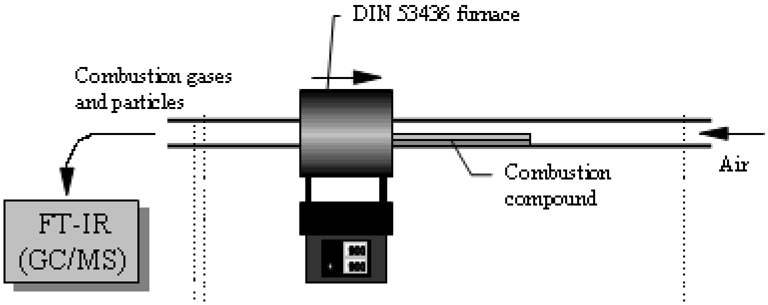


Figure 2. Setup of the DIN 53436 furnace [5].

2.1.2 Small-scale cone calorimeter

A modified ventilation-controlled cone calorimeter was used for the small-scale combustion experiments, Figure 3. The experiments were conducted at the Technical Research Centre of Finland (VTT) and the results are reported in [7]. Control of the ventilation was managed by placing the sample on a load cell 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.

2.1.3 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 4. The experiments were performed at the Department of Fire Safety Engineering, Lund University, Sweden. The results are reported in [9].

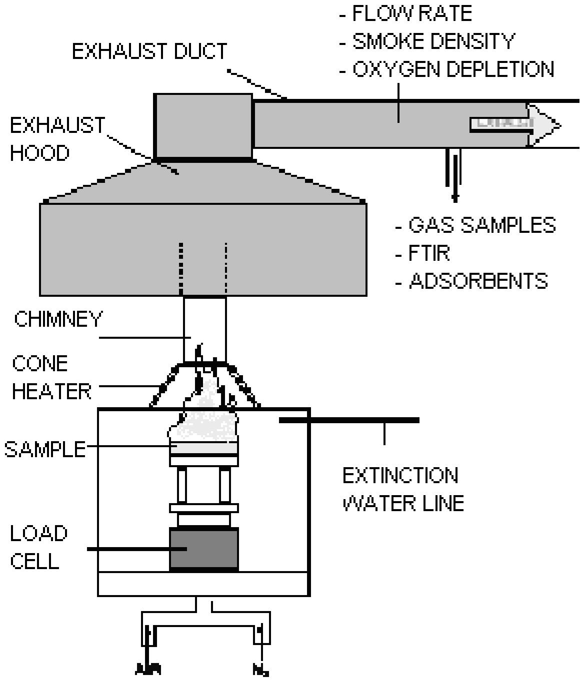


Figure 3. Setup of the cone calorimeter [7].

2.1.4 Indoor large-scale fire tests

The large-scale experiments were performed in a lightweight concrete room with dimensions in accordance with ISO 9705, as shown in Figure 5. The experiments were conducted at the Swedish National Testing and Research Institute (SP) and the results are presented in [8]. The room had one opening measuring 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, weighing 50 kg, was placed in pans of different sizes (0.5 - 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 fuel ratios, the scaling factors in the TOXFIRE experiments in micro-, small-, medium- and large-scale were 1 : 10 : 500 : 50,000.

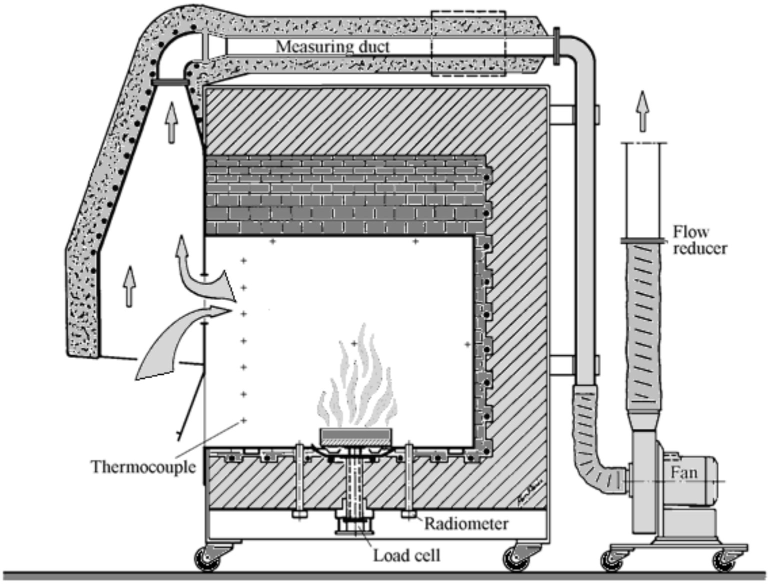


Figure 4. Setup of the 1/3 ISO room scale facility [9].

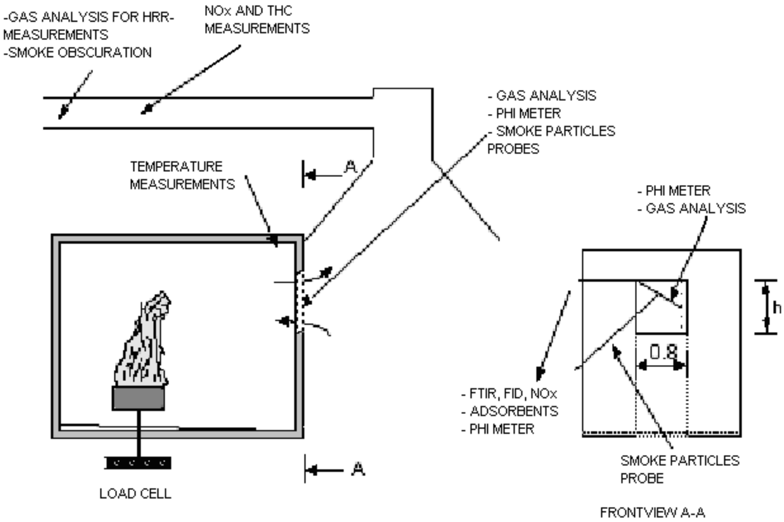
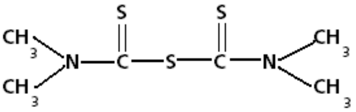
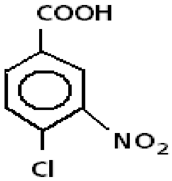
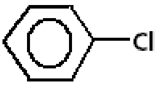
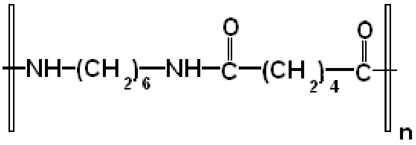
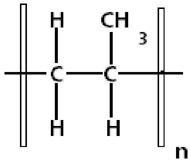


Figure 5. Setup of the ISO 9705 room facility, indicating the sampling probe configurations in the door opening and in the exhaust duct [8].

2.1.5 Studied chemicals

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 quantity of substance tested, 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 micro-scale experiments [5, 6].

Table 1. Substances studied in the TOXFIRE project, medium-scale.

Chemical	**Formula**
Heptane Heptane C_7H_{16}	**$CH_3\text{-}CH_2\text{- }CH_2\text{ -}CH_2\text{ -}CH_2\text{ -}CH_2\text{ –}CH_3$**
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 $-C_{12}H_{22}N_2O_2-$	 $\left[NH-(CH_2)_6-NH-\overset{O}{\overset{\parallel}{C}}-(CH_2)_4-\overset{O}{\overset{\parallel}{C}} \right]_n$
Polypropylene PP $-C_3H_6-$	 $\left[\underset{H}{\overset{H}{C}} - \underset{H}{\overset{CH_3}{C}} \right]_n$

In the medium-scale tests, six substances were tested. The tested substances are presented in Table 1 and some of their characteristic variables are given in Table 2. M_w is the molecular weight, Δh_c is the net heat of combustion and r_i is the stoichiometric air-to-fuel-mass ratio. Heptane was included as a fuel with well-known fire characteristics. Polypropylene, on the other hand was introduced as a "help" substance for ignition of substances that were difficult to ignite. It was chosen because it consists of only carbon and hydrogen and thus, should not contribute to combustion products containing hetero-atoms.

Table 2. Characteristic variables for the substances studied in the TOXFIRE project [12].

Substance	**M_w [kg/kmol]**	**Δh_c [kJ/kg]**	**r_i [kg_{air}/kg_{fuel}]**
Heptane	100.2	$-44.6 \cdot 10^3$	15.11
TMTM	208.4	$-25.7 \cdot 10^3$	7.91
CNBA	201.6	$-13.7 \cdot 10^3$	3.92
CB	112.6	$-26.2 \cdot 10^3$	8.54
Nylon 6,6	$226.3 \cdot n$	$-29.2 \cdot 10^3 \cdot n$	10.02
PP	$42.1 \cdot n$	$-43.3 \cdot 10^3 \cdot n$	14.7

2.2 Halon replacement agents

Experimental set-ups were designed in order to compare the efficiency of extinguishing agents and to determine their thermal breakdown products. Three different small-scale set-ups and one large-scale scenario were used:

- 8-litre bombs were used to determine the inerting concentration.
- A cup burner was used in which the extinguishing agent was mixed with air in varying proportions and introduced into a propane flame to find the extinguishing concentration.
- Thermal breakdown of the extinguishing agent was studied in an apparatus consisting of a tubular burner, where the extinguishing agent was mixed with the fuel in different ratios, in conjunction with calorimeter equipment.
- A large-scale enclosure was set up to study the extinguishing effect of one of the new halon replacement agents.

2.2.1 Inerting concentrations

Inerting concentrations and flammability limits of mixtures of fuel, extinguishing media and air can be determined in various types of apparatuses where the gases are contained in a closed vessel, mixed and ignited with an electric spark. In Figure 6, a flow chart of the equipment used is shown. In the experiments referred to herein a cubic pressure vessel with a volume of 8 litres was used. Fuel, extinguishing agent and air were fed into the evacuated vessel. The actual concentration inside the vessel was determined by measuring the partial pressure of the added gases. After thorough mixing of the gases with an internal fan for 10 minutes, the mixture was allowed to reach quiescent conditions over a 1 minute period. The switch to the capacitor was turned on and the capacitor discharged. A 5 µF capacitor with a potential of 11 kV, giving a stored energy of 30 J, was used to ignite the gas mixture. An oscilloscope was connected to the circuit in order to check the charging of the capacitor and also to see that there was no remaining charge after the discharge of the capacitor. The vessel was placed under a hood connected to an exhaust duct in order to allow all gases to be safely evacuated from the test room. The tests were documented on videotape and these recordings were studied to determine the inerting concentrations for the extinguishing agents studied.

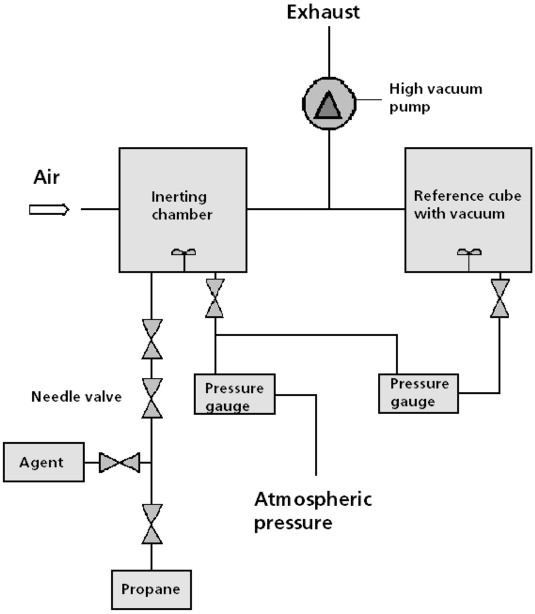


Figure 6. Flow chart of the equipment for determination of inerting concentrations.

2.2.2 Flame-extinguishing concentrations

The effectiveness of an extinguishing agent when used to extinguish small flames can be studied in different set-ups. The cup burner method is frequently used for this purpose. The key element in the method is a diffusion flame of a gaseous or liquid fuel which is centrally placed in a quartz tube. An air stream passes the flame and the extinguishing media being studied is added to the air stream. The amount of extinguishing agent is slowly increased until the flame is extinguished. This method has been standardized by a number of organisations and companies e.g. the International Organization for Standardization (ISO), Imperial Chemical Industries (ICI), and FM Global (former Factory Mutual Research Corporation (FMRC)). The apparatus used in the experiments presented here has dimensions corresponding to the FMRC cup burner. The burner has a diameter of 28 mm and the chimney has a diameter of 105 mm. Propane was chosen as the fuel.

In Figure 7 a flow chart is given for the equipment with flow meters attached. A small flow of the air/extinguishing agent mixture was drawn through an oxygen analyser to check the concentration of agent in the air flow.

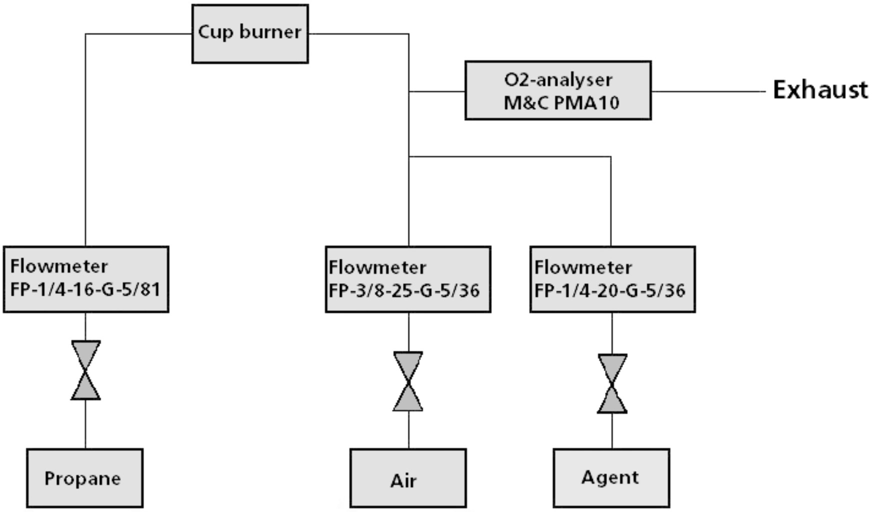


Figure 7. Flow chart of the equipment for determining flame-extinguishing concentrations.

2.2.3 Thermal breakdown products – Tubular burner method

In order to examine the thermal breakdown products which are produced when an extinguishing agent is applied to a fire an experimental set up was designed. Essentially, it consisted of a tubular burner of the McKenna type [13] (Figure 8) where the fuel, propane, was mixed with the extinguishing agent. The burner was cooled with water at about 10°C when a gaseous agent was used. For the experiments using a liquid agent, the "cooling" water had a temperature of about 40°C in order to ensure vaporisation of the agent. The burner was placed under the hood of a standard ISO 5660-1 cone calorimeter. The cone-shaped radiant heater was disassembled and the remaining parts of the calorimeter were used for collecting combustion products, gas analysis and smoke measurements. The experimental set-up is shown in Figure 9. The volume flow of gases through the exhaust pipe was approximately 20 l/s in all experiments. The flow was determined by measuring the pressure drop over an orifice plate, as well as the temperature of the exhaust gases. The smoke production was determined continuously in the exhaust pipe by measurement of the light extinction. The production of combustion gases was measured on-line. Oxygen, carbon monoxide and carbon dioxide were measured using conventional techniques. FTIR analysis was employed to analyse breakdown products as well as CO and CO_2.

Figure 8. The McKenna burner with propane flame under the hood of the cone calorimeter.

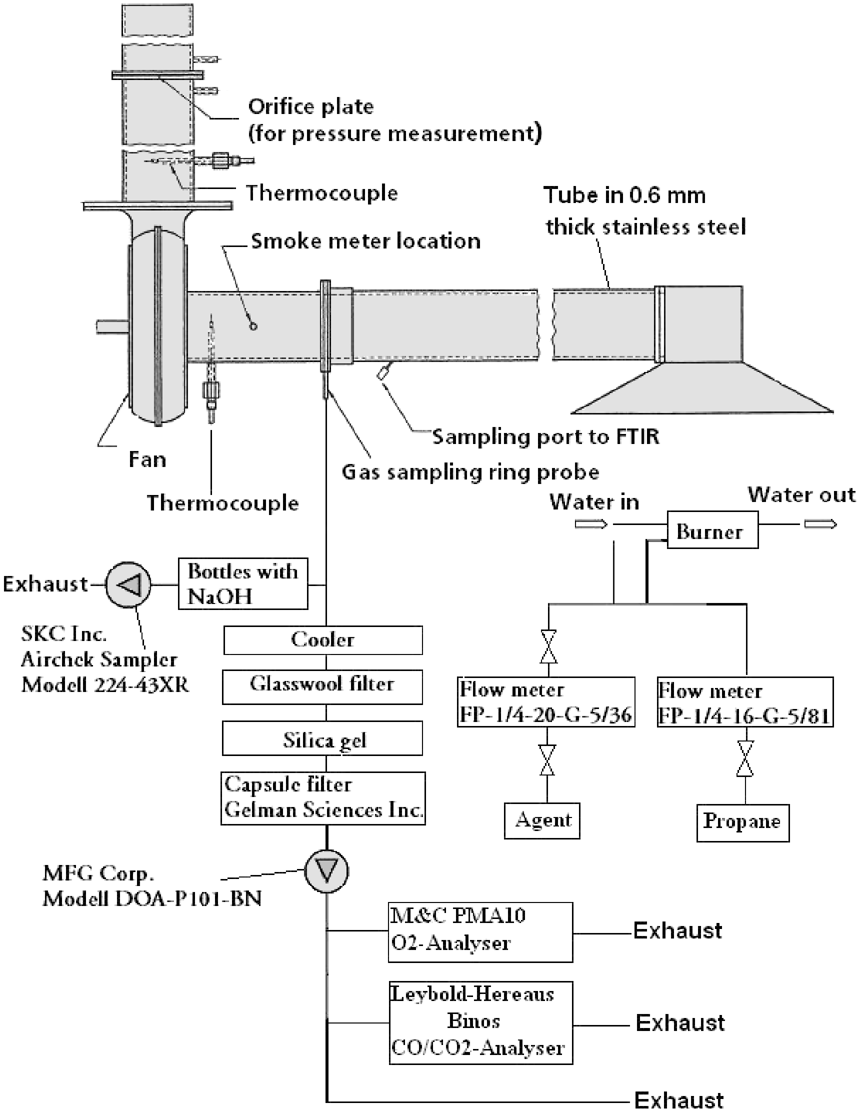


Figure 9. Flow chart of the experimental set-up for the experiments for determination of thermal breakdown products from extinguishing agents. (Illustration by Fei Tao.)

2.2.4 Large-scale experiments

Two large-scale experiments were performed in order to test the ability for one halon replacement agent to extinguish a small fire in a relatively large enclosure. The experiments are reported in [14]. The enclosure was an isolated steel container with a volume of 26.3 m^3 and the dimensions: 2.175 m (height), 2.2 m (width) and 5.5 m (length). Measurements were made of temperatures and production of hydrogen fluoride. The experimental layout is presented in Figure 10. In order to determine if the agent was able to extinguish a small fire two steel cabinets were placed at the far end of the container opposite the opening. One cabinet was equipped with a fan to simulate mechanical ventilation and the other just had natural ventilation of the fire gases. A fire was planted inside the cabinets. In the first experiment the fire was 1 kW and in the other 4.5 kW. The agent was introduced via a nozzle in the centre and 10 cm below the ceiling in the two cabinets respectively.

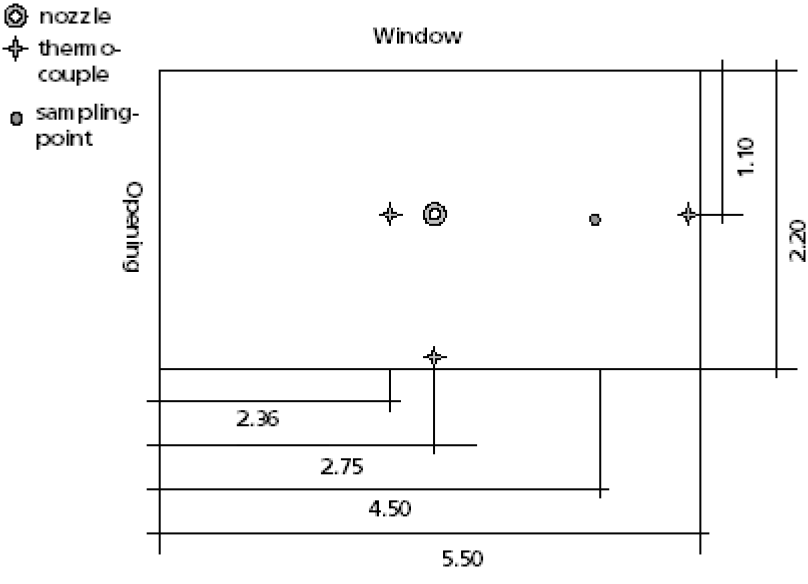


Figure 10. Layout of the large scale experiments with halon replacement agent.

2.2.5 Chemicals studied

A number of halogen-containing extinguishing agents were studied in order to find their characteristic extinguishing qualities. Their chemical compositions are presented in Table 3 and some characteristic variables are given in Table 4.

Table 3. Chemical composition of halon replacement agents.

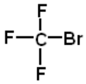
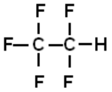
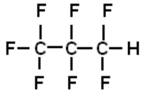
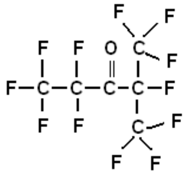
Substance	Chemical formula	Chemical structure
Bromotrifluro-methane Halon 1301	CF_3Br	
Pentafluoro-ethane HFC 125	C_2HF_5	
Heptafluoro-propane HFC 227ea	C_3HF_7	
Dodecafluoro-2-methyl-pentane-3-one C_6F-ketone	$C_6F_{12}O$	

Table 4. Characteristic variables for halon replacement agents.

Substance	Molecular weight	Boling point at 1 atm [°C]	Vapour pressure at 25°C [MPa]	Vapour density at 20°C, 1 atm [kg/m^3]
Bromotrifluro-methane Halon 1301	148.9[15]	-57.9[15]	1.62[15]	6.01[16]
Pentafluoro-ethane HFC 125	120.0[15]	-48.5[15]	1.37[15]	4.97[17]
Heptafluoro-propane HFC 227ea	170.0[15]	-16.4[15]	0.458[15]	7.26[17]
Dodecafluoro-2-methyl-pentane-3-one C_6F-ketone	316.0[18]	48.0[18]	0.04[18]	18.4[18]

The choice of agents was made in order to get a representative selection of halon replacements. Halon 1301 was included as a reference since there are a lot of published data available on this substance, see e.g. Babushok et al. [19].

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 summary of available measuring techniques used in this work is presented below.

3.1 Temperature and heat flux

The temperature inside a fire compartment and of the combustion gases leaving a fire is an important parameter when assessing fire hazards. The temperature is usually measured using thermocouples of different types. Bare-bead thermocouples, shielded thermocouples and aspirated thermocouples are types that are used frequently. The thermocouples can be of varying thickness and material.

It is sometimes of interest to know the total heat flux or the radiation towards a surface during a fire experiment. The total heat flux can be measured using e.g. a total heat flux meter of the Gardon [20] or the Schmidt-Boelter type [21]. Measurement of radiation towards a surface or a point in a fire room can be performed with a Gunners type radiometer [22]. In the TOXFIRE medium-scale experiments radiometers, of the Gunners type were used to measure the radiation towards the floor. This was done in order to determine the external radiation applied to the test samples inside the combustion chamber.

3.2 Yields of gases and particles

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. 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.

Combustion products can be characterised and presented in a number of ways. One way of presenting the results is 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.

3.2.1 TOXFIRE

Characterisation and quantitative analysis of the components in the combustion gases were essential parts of the TOXFIRE 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, HC and SO_2. The content of unburned hydrocarbons was also analysed on-line in the 1/3 ISO room and in the ISO room. These on-line gas measurements gave continuous data on the concentration of the low molecular weight combustion products. 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 [23].

Grab samples were taken of soot and combustion gases in order to analyse high-molecular-weight combustion products both qualitatively and quantitatively. The samples were analysed with a number of techniques including Fourier transform infrared spectrometry (FTIR), gas chromatography with flame ionisation and/or mass spectrometry techniques. The gas and soot samples were collected on adsorbing substrates, for example, XAD-2, Tenax or active carbon. These methods of analysis give the cumulated production of the components analysed over the whole sampling period.

One important purpose of these analyses was to determine that which 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.

During the TOXFIRE experiments, two different methods were used for on-line analysis. Conventional on-line instruments were used to determine O_2, CO_2, CO, NO_x and the amount of unburned hydrocarbons. In addition 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 5.

Table 5. 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 experiments	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

The FTIR technique offers the possibility of determining 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 [24], which was used by VTT (the Technical Research Centre of Finland) in small-scale tests in the TOXFIRE project [7]. 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. [25].

3.2.2 Halon replacement agents

In this project the production of combustion gases was measured on-line in the tubular burner experiments. Oxygen, carbon monoxide and carbon dioxide were measured with conventional techniques. Specifications for the measuring equipment are given in Table 6 [11].

Table 6. Specification of instruments used for gas analysis in the halon replacement project.

Measurement	**Equipment**	**Range, accuracy**	**Calibration gas**
O_2	M&C Type PMA 10, paramagnetic	0-100 vol. % ± 0.1 vol. %	21 vol. % 9.94 ± 0.200 %
CO	Leybold-Hereaus, Binos	0-1 vol. % ± 1 % of full scale	0.202 ±0.0040vol.% 202 ± 4.04 ppm
CO_2	Leybold-Hereaus, Binos	0-20 vol. % ± 1 % of full scale	4.99 ± 0.0998 vol.% 0.502 ± 0.010 %
HF, COF_2, HBr, etc.	FTIR, BOMEM MB-100	See page 43-44	See page 43-44

Other combustion products such as hydrogen fluoride, HF, carbonyl fluoride, COF_2, and hydrogen bromide, HBr, were analysed using FTIR. Samples for analysis of HF content, using ion chromatography, were also intermittently taken from the exhaust pipe. Further samples were taken on activated carbon sampling tubes in selected tests for subsequent GC-MS analysis of organic combustion products. Between 100 ml and 500 ml of smoke gases were sampled on each sampling tube. Several samples were taken in each test.

The instrumentation used for the FTIR measurements consisted of a FTIR spectrometer (Bomem MB-100) fitted with a multi-pass gas cell (Infrared Analysis M-38H-NK-AU).

3.3 Smoke Production

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 components. 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. Smoke measurements can be made either as static measurement; e. g. by collecting the smoke produced from a heated sample in a box and measuring the obscuration inside the box. It has become 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. This type of smoke measurement can be characterised as a dynamic measurement. 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. 2.

$$k = \left(\frac{1}{L}\right) \cdot \ln\left(\frac{I_0}{I}\right) \qquad \text{Eq. 2}$$

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. 3 from reference [26]:

$$k = \sigma_s \cdot C \qquad \text{Eq. 3}$$

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.

$$\sigma_f = \varepsilon \cdot \sigma_s \qquad \text{Eq. 4}$$

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 of soot particles produced. The value of σ_s is rather constant, about 10,000 m^2/kg, for flaming combustion of organic fuels [27]. σ_s can also be determined according to Eq. 5 from measurements in a duct and from samples of soot collected on filters during experiments.

$$\sigma_s = k \cdot \left(V \cdot \left(273 + T_{duct}\right)/273\right)/m_{soot} \qquad \text{Eq. 5}$$

V [m^3] is the volume of gas that has passed through the filter, T_{duct} [°C] is the temperature in the duct and m_{soot} [kg] is the amount of soot 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 follows:

$$S_{pr} = k \cdot \dot{V} \cdot \left(\left(T_{duct} + 273\right)/273\right) \cdot \left(1/\sigma_s\right) \qquad \text{Eq. 6}$$

The soot yield can then be calculated as the ratio between S_{pr} and σ_s.

3.3.1 TOXFIRE

Measurements were made of smoke density in the medium-scale experiments. The measurements were made using a lamp with a colour temperature of 2900±100 K and a photo-cell detector mounted in the exhaust duct. From these measurements, the values of σ_s and S_{pr} were determined for the substances studied in the TOXFIRE project.

3.3.2 Halon replacement agents

The smoke density was measured in the exhaust duct from the cone calorimeter. For this purpose, the standard equipment for smoke measurements in the cone calorimeter was used [28]. The smoke extinction coefficient was calculated and used for comparisons between the varying amounts of agents and different agents introduced into the flame.

3.4 Rate of heat release

The heat released by a material, normalised 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 [29]. 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 normalise the heat release rate since this quantity can be used for scaling purposes.

The heat released during an experiment can be calculated using the standard, oxygen consumption, calorimetric method, Eq. 7 and 8 [30, 31, 32]. Concentrations of O_2, CO_2 and CO can be used for the calculations. The volume flow $\dot{V}$ [m^3/s], at STP, in the duct, can be 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 typically in the order of 0.9. The calibration constant for the bi-directional Pitot tube [33] is 1.08.

$$\dot{V} = \frac{22.4 \cdot A \cdot 0.9}{1.08 \cdot \sqrt{\frac{\Delta p}{T_e}}} \qquad \text{Eq. 7}$$

The rate of heat release q [kW] can be calculated using the following expression:

$$q = \Delta H_{C,ox} \cdot 1.31 \cdot 1000 \cdot \frac{\phi}{1+\phi(\alpha-1)} \cdot \dot{V} \cdot X_{O_2}^0 \qquad \text{Eq. 8}$$

Where $\Delta H_{C,ox}$ [kJ/gO$_2$] is the heat released per unit mass of oxygen consumed. The value of $\Delta H_{C,ox}$ is assumed to be approximately constant for most combustible substances and materials. $X_{O_2}^0$ is the mole fraction of O_2 in the incoming air. In [34] Huggett gives a thorough survey of the heat of combustion for various types of substances and materials. It is concluded that the overall value can be set to 13.1 kJ/g O_2 in most applications. 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 below:

$$\phi = \frac{X_{O_2}^0 \cdot (1 - X_{CO_2}) - X_{O_2} \cdot (1 - X_{CO_2}^0)}{X_{O_2}^0 \cdot (1 - X_{O_2} - X_{CO_2})} \qquad \text{Eq. 9}$$

Where X_i^0 is the mole fraction of gas *I* in the incoming air and X_i is the mole fraction of gas *I* in the exhaust duct. $X_{O_2}^0$ is set to 0.209.

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

3.4.1 TOXFIRE

The amount of heat produced was measured during all experiments except for the micro-scale experiments in the DIN furnace [5]. The oxygen consumption, calorimetric method was used to monitor the heat output. From these measurements, the total energy released during each experiment could be calculated.

3.4.2 Halon replacement agents

In the project with halon replacement agents, the rate of heat release was measured in the experiments using the tubular burner. The main reason for the measurements was to study how the energy output changed when an extinguishing agent was added to the flame. The heat release rate was determined by the oxygen-consumption technique.

3.5 Degree of ventilation - 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 oxidiser-controlled fire, can be especially hazardous and life threatening. The production of CO is promoted by a low oxygen concentration, and because 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 are 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. 10. When the overall combustion process is studied the ratio is usually called the Global Equivalence Ratio (GER) often denoted as ϕ.

$$GER = \phi = \frac{\dot{m}_{fuel} / \dot{m}_{oxygen}}{\left(\dot{m}_{fuel} / \dot{m}_{oxygen}\right)_{stoich}} \qquad \text{Eq. 10}$$

A thorough presentation of the GER concept is given by Pitts [35]. 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 [36, 37]. However, LIF measurements include complex corrections for the sensitivity of the signal to collision partners and the use of Rayleigh scattering are 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 [38]. This apparatus has been developed further in order to make it more versatile and easier to use in nonlaboratory 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 is presented in Figure 11. The main part of the phi-meter is a heated steel reactor filled with a catalyst. A sample of a mixture of fuel gas and air is drawn through the heated reactor. The fuel gases are completely combusted in the reactor. To achieve this, a known amount of oxygen is added just before the inlet to the reactor. After passage through the reactor, the gases are cooled and stripped off water and CO_2 and then the content of oxygen is measured. The reactor can be heated up to 1100°C but temperatures in the range of 350°C to 600°C were found to be sufficient. The choice of catalyst is vital in order to achieve complete combustion in the reactor. Two different catalysts were tested. One was a metal oxide catalyst with oxides of Al, Cu and Mn. The other consisted of silica beads covered with platinum. It was concluded that both types of catalyst functioned well but that the Pt-catalyst needed a higher temperature in the reactor to provide complete combustion. A detailed description of the phi-meter is presented in Paper II.

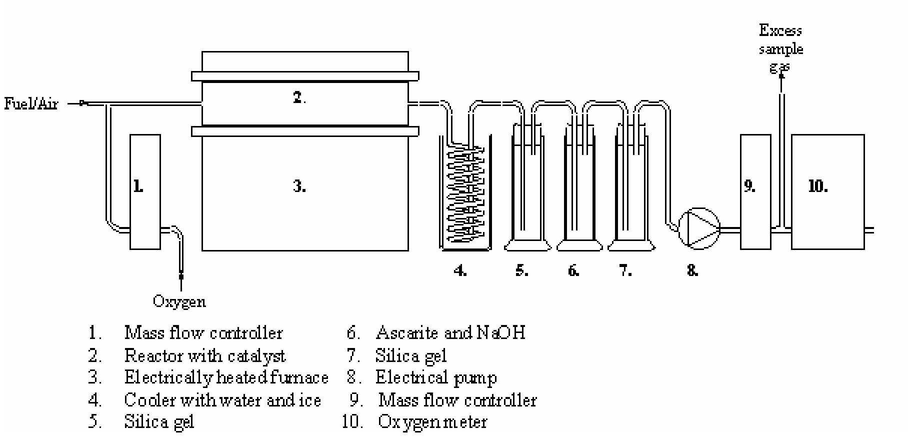


Figure 11. The overall layout in the phi-meter experiments.

In addition to measuring the GER, the phi-meter can be used to determine the local equivalence ratio of a specific location inside a room or in a flame. In order to investigate the versatility of the methods presented in Paper II, 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 12.

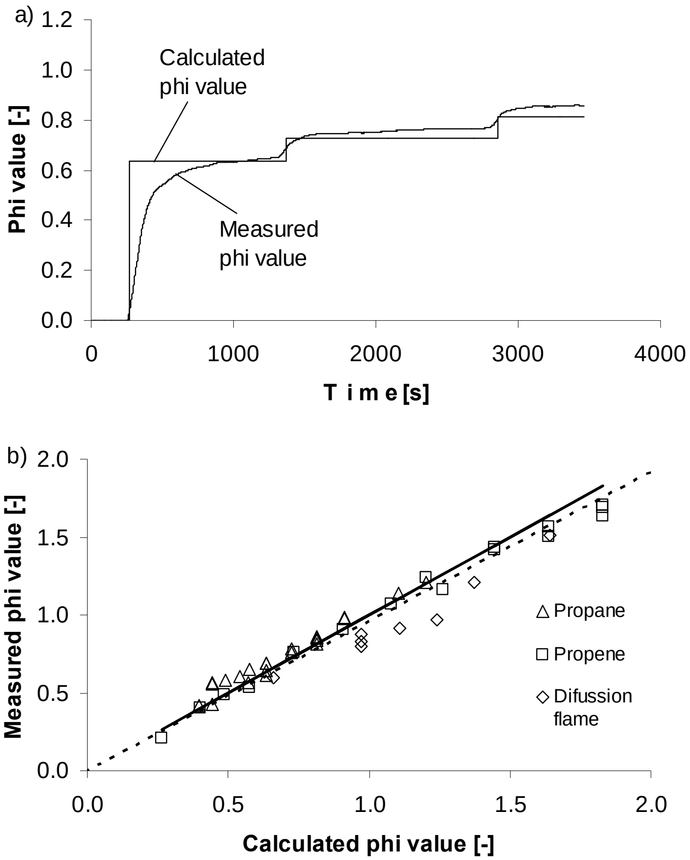


Figure 12. a) Measured and calculated phi values from an experiment on the combustion of propane, as a function of time.
b) Experimental versus calculated phi values for measurements using the phi-meter. Results for propane, propene and a propene diffusion flame are shown in the diagram. The solid straight 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.

A second technique for measuring the equivalence ratio was tested in connection to the phi-meter experiments. This technique 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. The nitrogen represents the amount of air in the sample and the carbon dioxide represents the amount of fuel. The phi value can be calculated as shown in Eq. 11.

$$\phi = \frac{p_{CO_2} / p_{N_2}}{(p_{CO_2} / p_{N_2})_{stoich}} \qquad \text{Eq. 11}$$

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 passing through 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' 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 introduced into the high-vacuum cell via the glass orifice, the pressure rises to approximately 10^{-3} Pa. A flow chart of the process is presented in Figure 13.

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. Results from experiments using this technique are reported in Paper II.

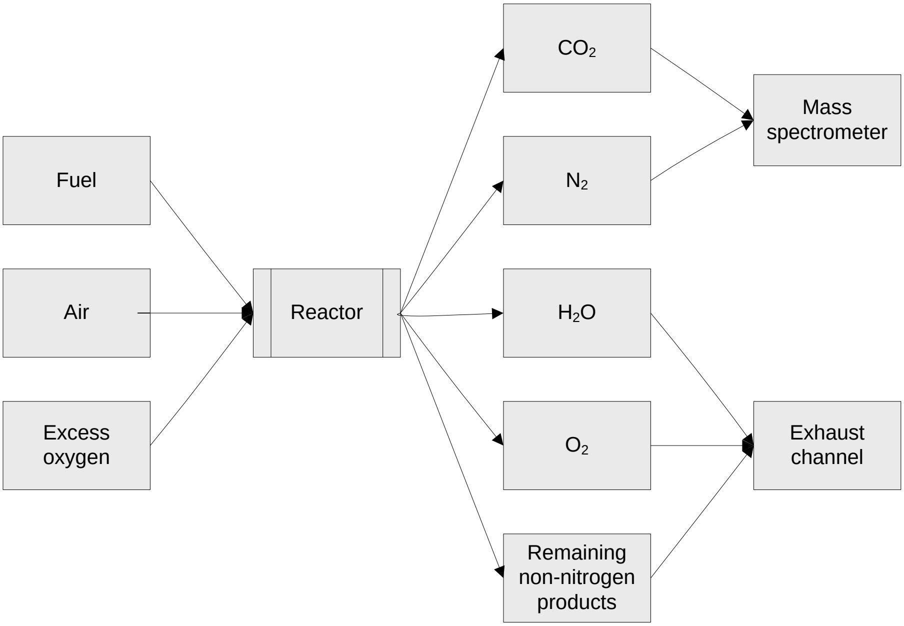


Figure 13. Flow of fuel and combustion gases for the analysis with mass spectrometer.

For the measurement of the GER in enclosure fires Gottuk [39] 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 side 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 [40] 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 normalised by the stoichiometric ratio.

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

$$\phi = \frac{S \cdot \dot{m}'' \cdot A}{\dot{m}_{air}} \qquad \text{Eq. 12}$$

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, e.g. Sivathanu and Faeth [41]. 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 [42, 43] and applied to fires involving polymer 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 [42]. The correlations for CO_2 (Eq.13), and CO (Eq. 14), are presented below:

$$\frac{(y_{CO_2})_{vc}}{(y_{co_2})_{wv}} = 1 - \frac{1.00}{\exp(\phi / 2.15)^{-1.2}} \qquad \text{Eq. 13}$$

$$\frac{(y_{CO})_{vc}}{(y_{CO})_{wv}} = 1 + \frac{\alpha}{\exp(2.5 \cdot \phi^{-\xi})} \qquad \text{Eq. 14}$$

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 conventional way to determine the GER is to measure the fuel mass loss, opening size and temperature of the air entering the combustion enclosure and the temperature of the upper gas layer, and calculate the GER as follows [44, 45]:

$$\phi = \frac{m_{fuel} \cdot \left(1 + \left(\frac{T_g}{T_a}\right)^{1/3}\right)^{3/2}}{\frac{2}{3} \cdot h^{3/2} \cdot w \cdot C_d \cdot \sqrt{2 \cdot g} \cdot \rho_0 \cdot \left(1 - \frac{T_a}{T_g}\right)^{1/2} \cdot r} \qquad \text{Eq. 15}$$

In the equation above r is the stoichiometric fuel/air mass ratio, h is the height of the opening, w is the opening width, C_d (0.68, [46]) is a discharge coefficient and g is the gravitational constant. T_a is the ambient temperature; T_g is the mean gas temperature in the upper layer of the combustion enclosure and ρ_0 is the density of the surrounding air. The above expression applies when the fire enclosure has one opening. For enclosure with multiple openings it can not be used.

3.5.1 TOXFIRE

In the TOXFIRE project the equivalence ratio was measured using the phi-meter in the modified version described in Paper II. The degree of ventilation was also measured in a more conventional way from measurements in the opening of the combustion enclosure. An example of measured and calculated GER is given in Figure 14 for an experiment with TMTM, in the 1/3 scale ISO room, within the TOXFIRE project. The "Tewarson" approach described in the preceding section was applied to the chemicals studied in the TOXFIRE project and some results are presented in section 5.1.

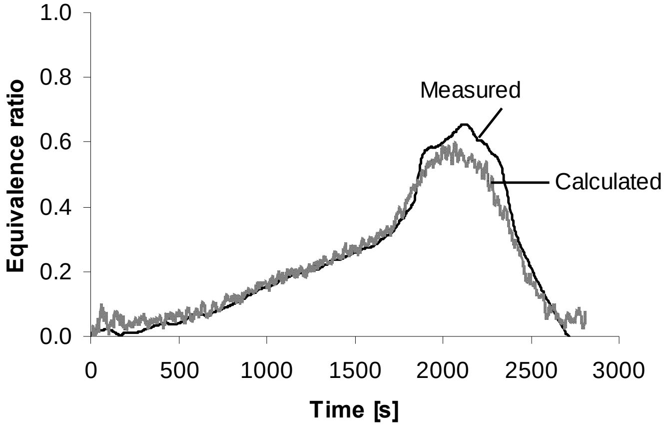


Figure 14. Measured and calculated global equivalence ratio from a TOXFIRE experiment with TMTM in the 1/3 scale ISO room.

3.5.2 Halon replacement agents

The degree of ventilation was not measured in this project since all experimental configurations except the large-scale scenario were made in the open with full access to oxygen. The idea is that the fire should be extinguished early during its development and therefore there is no influence on the oxygen concentration.

4 Limitations in measurement techniques

The performing of fire experiments generally includes measurement of different types of variables that can be used in order to characterise the course of the fire. A measurement process gives a number which gives information about the magnitude of the measured variable. The question is how good this information is. Is it a crude estimate or is it really a correct value? The measured value is influenced by many factors such as the instrument used for the measurement, the accuracy of the calibration of the instrument, environmental factors at the time of measurement. Human factors must also be considered.

When a measurement is performed it is assumed that the quantity measured has an exact value but that the measurement will not always present this true value. A measurement error will have to be taken into consideration. This error can be expressed as:

$$e = \frac{X_m - X_t}{X_t} \qquad \text{Eq. 16}$$

X_m is the measured value and X_t is the true value [47].

Errors can be divided into systematic errors and random errors. It is possible to reduce the influence of random errors by increasing the number of measurements performed. It is therefore important to make multiple experiments whenever this is feasible. Of course there are instances when this is not possible due to economic factors or lack of available material or products, for example.

When multiple experiments are performed the mean value, $\overline{X}$ and the standard deviation, σ^2 can be calculated according to Eq. 17 and 18.

$$\overline{X} = \frac{1}{N}\sum_{n=1}^{N} X_n \qquad \text{Eq. 17}$$

$$\sigma^2 = \frac{1}{N-1}\sum_{n=1}^{N} (X_n - X_t)^2 \qquad \text{Eq. 18}$$

Calculating a mean value might give a value which differs from any of the actually measured values but when $N \rightarrow \infty$, $\overline{X} \rightarrow X_t$. In reality

$N \neq \infty$ but $\overline{X}$ anyhow is a better estimate of the true value than a single measurement.

In real fires and in fire experiments, a further complication is introduced since the combustion in these cases is mainly turbulent. This means that the flow in the combustion zone or flame changes direction over time. The velocity also changes resulting in changes in density, temperature and mixing of the combustion components. This can be illustrated as in Figure 15 where an example of the fluctuations of a flame is given.

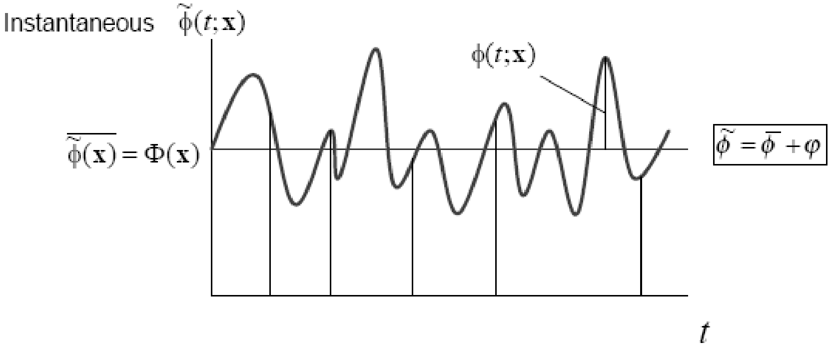


Figure 15. The curved line in the diagram illustrates how the position of a flame fluctuates over time. $\overline{\phi}$ represents the mean value of the flame position over time, φ is the change in fluctuation and $\tilde{\phi}$ is the instantaneous position of the flame.

The characteristics of systematic errors are different and can not be overcome by performing multiple experiments. If an experiment is repeated the measurement of a chosen variable will give a systematic error with the same value and sign every time the measurement is made, providing the measurement is performed with the same equipment and under the same conditions every time. It is sometimes possible to identify the systematic errors and they can then be accounted for in the final results from the measurements. It has been customary to present measurement results with indications of measurement errors insofar as is possible. During the last part of the twentieth century, it became more and more common to present measurement uncertainties instead of the magnitude of the measurement errors. This change was given a more official stamp by the publication in 1992 of the IEC-ISO "Guide to the Expression of Uncertainty in Measurement" [48]. Other organisations and authorities have also published guidelines to the same effect e.g., the National Institute of Standards and Technology (NIST) [49].

4.1 Temperature and heat flux

As mentioned earlier, measurement of temperatures at various locations during a fire experiment or test is an important indicator for the development of the fire. Temperature measurements are often made with thermocouples of different types. The material in the thermocouple can be chosen to suite the temperature range within which measurements will be made. In the fire experiments referred to in this document, bare-bead thermocouples of chromel alumel type have been used. The diameter has typically been 0.25 mm. They are suitable for temperatures up to 1000°C and the accuracy of the wire is reported by the manufacturer to be ± 0.4 %. A main disadvantage with thermocouple-based measurements is that it is an intrusive method which influences the flow field of the combustion gases. There are also such effects as catalytic reactions at the surface of the thermocouple and conductive heat losses via the wires. These latter are probably of minor importance in fire experiments. The influence of incident radiation is a greater problem. The thickness of the thermocouple wire is of course important when it comes to how well it can reproduce the temperature at a given point. 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. Methods for making corrections for the influence of radiation are available. Investigations on how well temperatures are reproduced by different types of thermocouples are presented in [50, 51] to name a few. In Figure 16, an example is given of the relation between the temperature measured and the diameter of the thermocouple. It is evident that the thicker thermocouple gives a higher temperature than the thinner thermocouple. This is mainly due to the influence of radiation on the thermocouple. The actual temperature is even lower than that given by the thinner thermocouple and can be estimated by performing measurements with thermocouples of varying diameters.

Non-intrusive methods for temperature measurements are available but have not been used in the experimental series referred to here. CARS-spectroscopy and laser-induced fluorescence are two methods that can be used for non-intrusive temperature measurements [52].

Together with temperature measurements, the estimation of the incident heat flux towards a surface or a material is an important variable in fire experiments. A total-heat-flux gauge measures the total incident heat flux towards a specific surface, namely a cooled thin metal foil. This gives rise to problems such as convective cooling at the surface and possibly condensation at the cold surface. To ensure measurement results of good quality, a standardised calibration procedure for heat-flux gauges has been adopted by ISO [53, 54]. As part of arriving at a standard for calibration, two round robins were undertaken [21]. Five fire laboratories took part in these round robins in which two types of heat-flux gauges, Gardon and Schmidt-Boelter, were used in the calibrations.

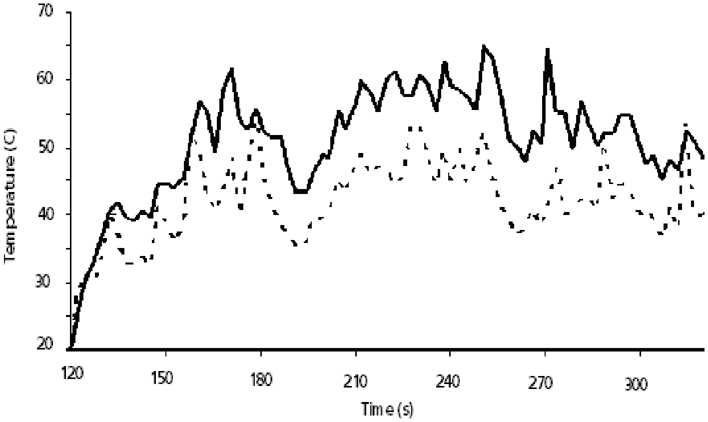


Figure 16. The diagram shows temperatures measured with two different thermocouple thicknesses, 0.25 mm (—) and 0.1 mm (---). The temperatures were measured in a ceiling jet at a distance of 2.5 m from a 1.1 MW propane flame (1 m^2), 0.15 m under a 5 m high ceiling.

The heat-flux meters used in the TOXFIRE project were of the Gunner’s type and measured only radiation towards the floor in the combustion chamber. The main draw back with these meters is that they measure the radiation from a limited part of the spherical volume surrounding the radiometer. The meters were calibrated using the spherical black-body cavity method. That is method 2 in the ISO document [54]. According to this document, the uncertainty in the calibration is less than 3 %.

4.2 Yields of gases and particles

Yields of gases and particles were measured in all scales within the TOXFIRE project. Since the experiments were performed at different laboratories, somewhat different equipment was used for the gas analyses. Much effort was put into designing the experiments in such a way that the results would be relevant for purposes of comparison.

The accuracy of the conventional on-line instruments is typically 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 be within the calibrated concentration range. The different types of instruments require different forms of preparation of the combustion gases prior to introduction into the instrument. All gas samples taken for gas analysis were taken using various probes. These are all extractive techniques and are subject to the same kinds of problems. The probes were typically made of metal or a polymer material. The probe can be either cooled or introduced into the stream of combustion gases without cooling. These different techniques can cause problems such as surface reactions on the probe or ongoing gas phase reactions after the extraction. These types of extractive sampling require a range of pre-treatments prior to introduction of the gas sample into the gas analyser. These 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. In Table 7, an example is given of instruments used for gas analysis, calibration gases used, measurement ranges and their accuracies. The examples are from the experiments in medium-scale.

Table 7. Gas analysis equipment for continuous measurements in the TOXFIRE medium-scale experiments.

Measured substance	**Analysis equipment**	**Range/ Accuracy**	**Calibration gas**
O_2	Siemens Oxymat 5E paramagnetic	10-21 vol. % ±1 % of full scale	20.9 vol. % 9.94±0.200 %
CO	Siemens Ultramat 22P, non-dispersive IR-absorption	0-1 vol. % ±1 % of full scale	0.202±0.0040 vol.% 202±4.04 ppm
CO_2	Siemens Ultramat 22P, non-dispersive IR-absorption	0-20 vol. % ±1 % of full scale	4.99±0.0998 vol. % 0.502±0.010 %
NOx	Analysis Automation Ltd. Chemiluminiscens analysis, model 443	0-100 ppm ±1 % of full scale	93.6±1.9 ppm
HC	Siemens Fidamat K FID	0-100 ppm ±1 % of full scale	50.9±1.0 ppm propane

The gas analyses in the project with halon replacement agents were made on-line with the equipment described in Table 6, page 26. In addition continuous analyses were also made with FTIR. The instrumentation used for the FTIR measurements consisted of a FTIR spectrometer (Bomem MB-100) with a multi-pass gas cell (Infrared Analysis M-38H-NK-AU). The FTIR spectrometer was used with a spectral resolution of 4 cm^{-1}. The information obtained was in the wave number range between 4500 cm^{-1} and 400 cm^{-1} and was stored in three consecutive scans which were combined to produce a new averaged spectrum every fifteenth second. A DTGS (deuterated triglycide sulphate) pyroelectric detector was used to measure the infrared beam after passing through the cell. The gas cell, which had a volume of 0.922 dm^3 and a path-length of 4.8 m, was heated by a cylindrical heating element to maintain a constant temperature of 150°C. The smoke gases were continuously drawn to the FTIR with a sampling rate of 4 l/min using a probe with a cylindrical ceramic filter (M&C 2 μm) mounted in the exhaust duct of the cone calorimeter. Both the filter and the gas sampling line (4 mm I.D. PTFE) were heated to 180°C. The FTIR was quantitatively calibrated for: hydrogen fluoride (HF) in the concentration range 0 – 1000 ppm, carbonyl fluoride (COF_2) in the range 0 – 1085 ppm, and hydrogen bromide (HBr) in the range 0 – 1000 ppm. The FTIR was further quantitatively calibrated for CO_2, CO and HCl (Paper III).

In the SAFIR project (Smoke Gas Analysis by Fourier Transform Infrared Spectroscopy) within the European Standards, Measurement and Testing programme gas analysis of smoke gases with FTIR was further developed. The objective of the project was to improve the technique, making it a more reliable measuring method for gas analysis of hot gases from combustion and fire experiments [25]. In this project, it was concluded that FTIR analysis of combustion gases is a suitable method as long as care is taken in the choice of calibration concentrations and the analysed gas sample is representative of the produced smoke gases.

The methods used for measuring species concentrations in the projects referred to here were all extractive methods of different types. There are other types of possibilities when measuring concentration of combustion products. Among these, Raman-spectroscopy, CARS-spectroscopy and laser induced fluorescence can be mentioned. They are all non-intrusive optical methods [52]. It should also be mentioned that no measurement of free radicals were made in the current projects.

4.3 Smoke production

The measurement of smoke production often consists of a number of combined measurements and thus the accuracy of the result is dependent on a number of measured variables. Among these are: mass flow in the duct, gas temperature at the measuring point and accumulation of soot on the optical lenses. All components involved in the measurement process have their own features, and in order to estimate the accuracy of the resulting smoke production, all these characteristics must be estimated. Methods for calculating the total uncertainty for smoke production measurements are presented in [55, 56], for example. Both articles report relatively high values for the measurement uncertainties, 10-20 % are not unrealistic values. In [55] it is especially emphasised that when products or materials that produce small amounts of smoke are tested, the uncertainties in the smoke measurements tend to be very high.

As mentioned in section 3.3, soot production can also be measured by extractive measurements in which soot is collected on filters and the mass of the collected soot particles is determined. In this type of measurement, the soot may, for example, adhere to the walls in the combustion device or along the sampling line. This will tend to give a lower value of soot production than the actual production.

4.4 Rate of heat release

The measurement of the rate of heat release (RHR) involves a number of different types of measurements with associated calibration constants and variables. This can be clearly seen in equations 7, 8 and 9 in Section 3.4. A number of researchers have given the subject of uncertainties in RHR-measurements attention. Results and opinions are presented for experiments in different configurations. Enright and Fleischmann [57] focuses on uncertainties linked to the method for calculating RHR in the cone calorimeter equipment. They emphasise that the uncertainty of the calculated RHR is strongly dependent on the chosen value for the heat released per unit mass of oxygen consumed. This is, of course, true for all situations where RHR is measured using the oxygen consumption technique. If the fuel is well known, the correct value of $\Delta H_{C,ox}$ should be used. The quality of the results from the oxygen analyser also highly influences the results. In addition Yeager [58] and Axelsson et al. [55] discuss uncertainties in measurement of volume flow and mass flow. Axelsson et al. present a combined expanded relative standard uncertainty for the measurement of RHR of 7-10 %. The importance of high-quality flow measurements is also stressed by Sette et al. [59]. The influence of the response time of the measuring devices employed is also discussed. Bryant and Mulholland [60] along with others discuss the influence of the different elements in the measurement of RHR. Their results show that for full-scale experiments, the uncertainty in determining the calibration constant for the bi-directional probe contributes significantly to the total uncertainty of the measurement of RHR. This is especially apparent in experiments with relatively high heat release rates. For low heat release rates, the uncertainty of the output signal from the gas-measuring instruments becomes more noticeable.

It can be concluded that the scale of the amount of heat released is highly dependant on the size of the experimental scale. Since the measurement of small variations in oxygen concentration is difficult, it is imperative that the hood arrangement for collecting the combustion gases be well adjusted to the experimental set up used.

5 Experimental results and experiences

In order to investigate the production of combustion gases when chemicals come in contact with high temperatures they can either be exposed to a fire or introduced into a flame as extinguishing media. In order to obtain knowledge of the kind of combustion products that can be expected, experiments can be conducted. Experiments can be performed in many different ways and scales. The production of combustion gases are influenced of the surroundings, e.g. an open configuration with free access to oxygen, a compartment fire or an experiment conducted under a hood. The composition of the combustion gases is a result of the involved chemical reactions and thus of the influencing parameters such as temperature, pressure, available amount of oxygen and also of the fluid dynamics of the combustion gases. It is difficult to fully understand and model what happens in a turbulent flame or in the fire plume in a compartment, but this can be at least partly understood by studying the chemical kinetics of the involved reactions.

Many attempts have been made to correlate measurements of combustion gas concentrations in the fire plume or in the upper gas layer in an enclosure fire with GER [42, 61, 62]. Pitts [63], 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. The composition of the combustion gases can be considerably altered by:
    - 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.

Tolocka et al. [64] have also shown experimentally that the yields of combustion gases are dependent on GER and temperature. They presented experimental results showing the dependence of the equivalence ratio on combustion products. This confirms former results [61], i.e. that CO increases with the equivalence ratio, and CO_2 increases with the equivalence ratio up to GER=1 and then decreases. They also found a pronounced temperature dependence indicating that the equivalence ratio 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 and in the project with halon replacement agents were of a more complex nature. See Tables 1, 2, 3 and 4 for descriptions of the substances and their characteristics.

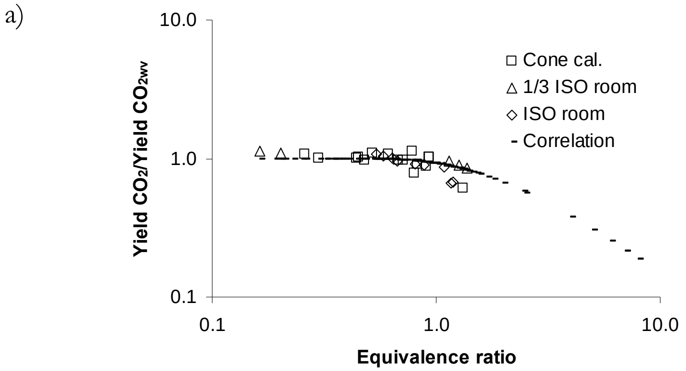
In the following sections, results from experiments using organic chemicals, most of which contain hetero-atoms, will be presented. Experiments in different scales and under varying conditions were performed.

5.1 Production of CO_2, CO, hydrocarbons and soot

In the TOXFIRE project experiments involving organic fuels containing hetero-atoms, observations regarding the dependence of the yields of CO_2 and CO on the equivalence ratio were similar to those reported by other researchers. This is illustrated by Figure 17 a), 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 equivalence ratio. The correlation according to Tewarson [42] is also shown. The correlations are given in Eq. 13 and 14 on page 36. In experiments with chlorine-containing substances, this relationship was much weaker, as can be seen for CNBA in Figure 17 b). For CNBA, the maximum yield of CO_2 was set to 1.53 kg/kg. As illustrated in Figure 17 b), the Tewarson correlation does not fit the data for this chlorine-containing substance.

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 equivalence ratio in Figure 18 a). The maximum yield of CO for well-ventilated conditions was assigned a value of 0.03 kg/kg. In Figure 18 b), the CO yield versus the equivalence ratio 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 CO yield, but this is not as evident for CB.

In the experiments with halon replacement agents, the main effort was put into measurement of halogen-containing combustion or breakdown products. Results from the measurements are presented in Paper III and in [11]. However, some results from the measurements of CO_2 and CO are reproduced here in Figures 19 and 20. The curves labelled $CO_{2,tot}$ and CO_{tot} show the concentrations measured as a function of time during extinguishing tests with the different extinguishing agents, respectively. The curves labelled $CO_{2,agent}$ and CO_{agent} show the difference between the concentrations in the extinguishing test and the concentrations from the combustion of the pure fuel at the beginning of each test. The difference can be regarded as the contribution from the extinguishing agent in emitted CO_2 and CO (which could be positive or negative), and originates from the influence of the extinguishing agent on the fuel combustion process and also of that of the reaction between the agent and oxygen. In Figure 19 a), results from a test with Halon 1301 are presented. The negative concentration for CO_2 shows that when Halon 1301 is added to the flame, the concentration of CO_2 decreased, and since the $CO_{2,agent}$ value is a calculated value this shows up as a negative concentration.



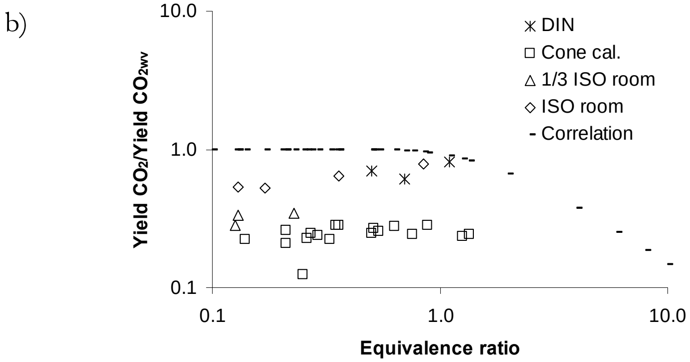
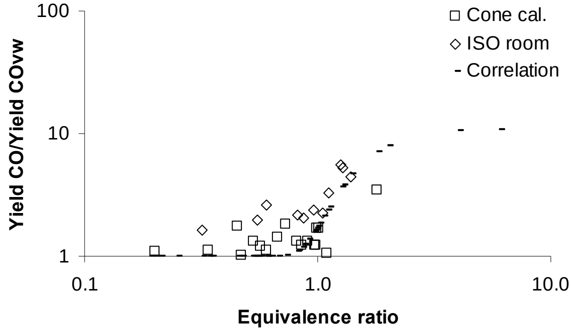


Figure 17. a) Ratio of the yield of CO_2 to the maximum yield of CO_2 for well-ventilated conditions in experiments with Nylon 6,6. The dashed line shows the Tewarson correlation.

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

a)



b)

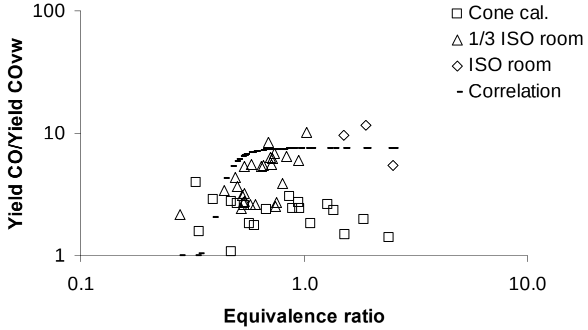
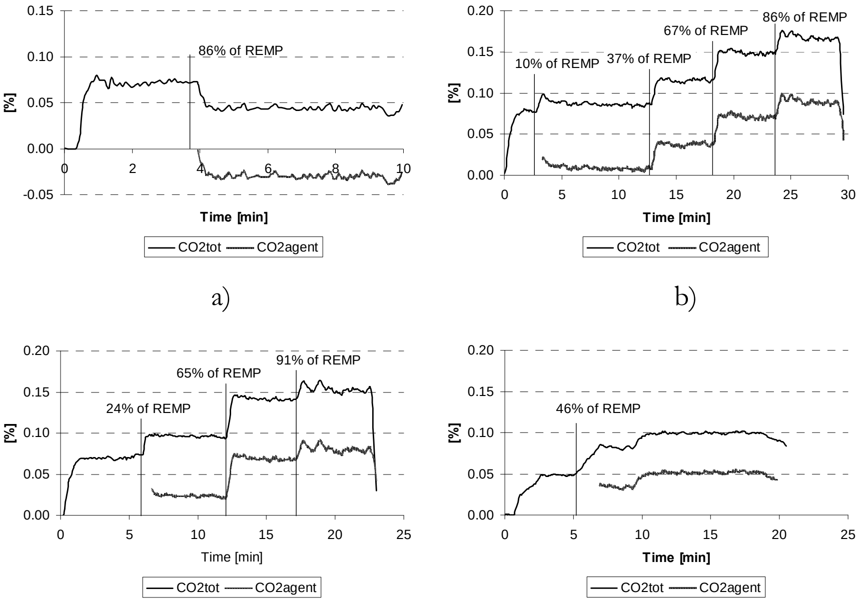


Figure 18. a) Ratio of the yield of CO to the CO yield for well-ventilated conditions during experiments with PP. The dashed line shows the Tewarson correlation.

b) Ratio of the yield of CO to the CO yield for well-ventilated conditions during experiments with CB. The dashed line shows the Tewarson correlation.

The production of CO_2 is highly dependent on the added amount of extinguishing agent. This can be clearly seen in Figure 19 b) and c) where the CO_2 production in experiments with HFC 125 and HFC 227ea are presented. The upper curve indicates the total amount of CO_2 produced and the lower curve gives the amount of CO_2 coming from the added extinguishing agent. As expected the fuel also contributes to the production of CO_2 and this is also evident in Figure 19.

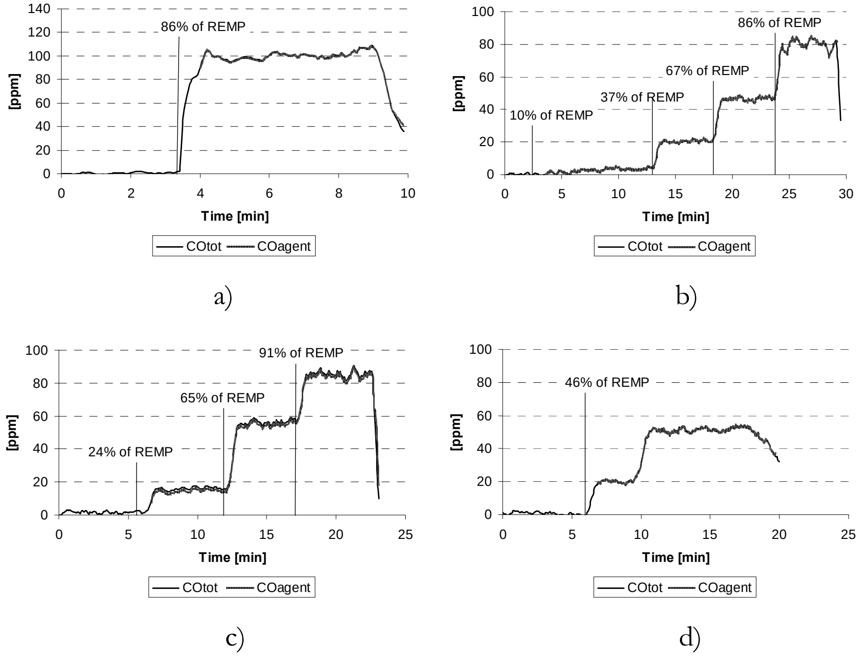


a) b)

c) d)

Figure 19. Production of CO_2 as a function of time, a) test 2 with Halon 1301, b) test 1 with HFC 125, c) test 2 with HFC227ea, d) test 3 with C_6F-ketone.

It was found that for all four agents, the production of CO originates mainly from the action of the extinguishing agent, and not from the normal combustion of the fuel. In Figure 20 showing the CO concentrations, it is difficult to see any difference between the two curves. This indicates that all CO produced comes from the influence of the extinguishing agent. This is expected as the function of the extinguishing agent is to interfere with the combustion process. Also the production of CO_2 is highly dependent on the amount of extinguishing agent added, which implies that the extinguishing agent takes part in the combustion process and contributes to the amount of heat released from the flame. In should be mentioned that the first plateau in Figure 19 and 20 d), a test with C_6F-ketone, is due to a problem with the addition of the liquid agent because of the vaporisation of the agent.



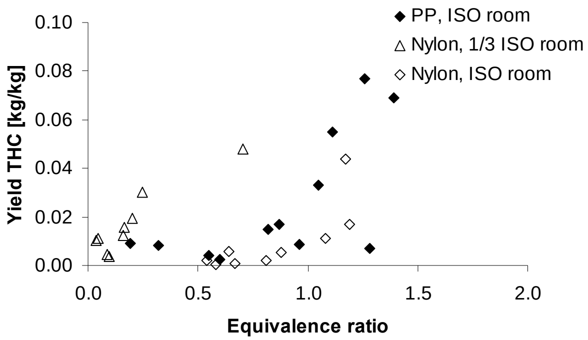
a) b)

c) d)

Figure 20. Production of CO as a function of time, a) test 2 with Halon 1301, b) test 1 with HFC 125, c) test 2 with HFC227ea, d) test 3 with C_6F-ketone.

In fires involving organic substances such as those studied in the TOXFIRE project, varying amounts of unburned hydrocarbons and soot are released along with the fire gases. Low-molecular-weight hydrocarbons can be measured on-line with conventional methods, but 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 21 a), the yields of unburned hydrocarbons increase as the degree of ventilation decreases. For CB, which contains chlorine, the results are different, Figure 21 b), and the trend is quite the opposite.

a)



b)

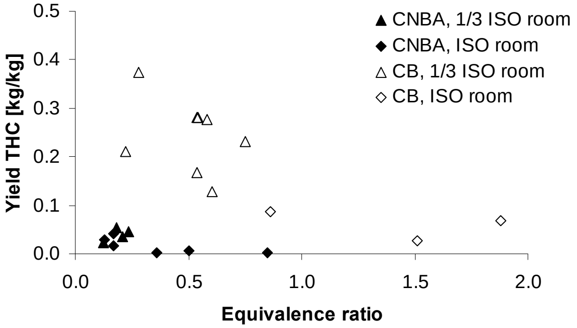


Figure 21. a) The yield of unburned low-molecular-weight hydrocarbons is presented as a function of the equivalence ratio for experiments with PP and Nylon 6,6.
b) The yield of unburned low-molecular-weight hydrocarbons is presented as a function of the equivalence ratio for experiments with CNBA and CB.

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 using a GC-MS fitted with a flame ionisation detector. Polymers behave somewhat differently, from many other organic substances, when heated. 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 oxidised. 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 GC-MS spectroscopy. This type of analysis may be qualitative or quantitative. Results from such analysis within the TOXFIRE project are presented in [9]. It was found that for some substances part of the parent substance was not affected at all by combustion and 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.

Since 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 these yields are dependent on the physical and chemical properties of the compound burned and the combustion conditions. In the TOXFIRE experiments measurable survival fractions were detected in the tests with CB and CNBA. These survival fractions are given in Table 8. The experiments with CB gave very large amounts of unburned compound. To be able to predict survival fractions of other compounds, the physical and chemical properties of the compound studied must be examined as described below. This is particularly important for toxic compounds, such as herbicides and pesticides.

Table 8. Survival fractions in % for CB (chlorobenzene) and CNBA.

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 total hydrocarbon content, 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 [65]. 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. All bond energies within the CB molecule are high compared to many other substances. The CNBA molecule has a nitro side group attached, and thus has lower bond energy within the molecule.

The next stage of combustion will involve reactions between free radicals and the compound. Thus, the reaction rates of the main radicals; OH·, H·, HOO· and others important for the oxidation process must be slow in relation to the residence time of the molecule in order to yield high survival fractions. 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. Furthermore 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 [62] 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.

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. [7]. 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.

In the halon replacement project, the main efforts were put into finding halogen-containing substances so no characteristic results can be presented concerning common hydrocarbons. However some breakdown products were identified in the FTIR measurements and it was also found that at high application rates, the IR-spectrum shows peaks which seem to come from the original extinguishing agent. In Figure 22 a) the spectrum from pure HFC 227ea is presented and in Figure 22 b), the spectrum for an application rate at 91 % of the REMP is given. The flame is thus close to extinction and the peaks from the pure agent are not easily distinguishable. Instead, peaks from HF, CO_2 and from COF_2 dominate the spectrum. There are also a number of peaks in the 91 % REMP spectra indicating survival fractions of the extinguishing agent. The peak at 1027 cm^{-1} is the major peak. The 1027 cm^{-1} peak is probably from an organic breakdown product. The molecular vibration responsible for the peak has not been identified, but it seems reasonable that it is some type of C-F vibration. As an example, the C-F stretch in CH_3F gives a peak at 1049 cm^{-1}. This type of analysis was also made for the other extinguishing agents and is presented in Paper III and in [11].

During combustion, soot is also produced in varying amounts depending on the substance burnt. The production of soot has not been a main issue in any of the projects that are referred to here but measurements of transmittance were made in both the TOXFIRE and the halon replacement projects. In TOXFIRE, collection of soot on filters for determination of mass production of soot was also made. Results from experiments in 1/3 scale room experiments in TOXFIRE are presented in Figure 23. As can be seen the amount of soot is highly dependent on the equivalence ratio. This can be expected since at low equivalence ratios, the amount of oxygen available for combustion is low thus yielding a great deal of non-combusted substances. Comparison with soot measurements in the other types of experiments within TOXFIRE is not meaningful since the results in the different configurations are presented in differing ways.

Transmittance was also measured in the halon replacement project but no mass loss was registered due to the design of the experiments. This precludes the calculation of soot yields. Examples of the normalised transmittance in experiments with the extinguishing agents tested are presented in Figure 24. The overall conclusion from these results is that the extinguishing agent takes part in the combustion process. As can be seen in Figure 24, from Paper III, the smoke production increases when the extinguishing agent is introduced into the propane flame. As shown in Figure 24, this behaviour was observed for all four agents. For HFC125 and HFC227ea, Figures 24 b) and c) show the normalised smoke transmittance for the entire range of REMP up to extinguishment of the flame. As extinction is approached, the transmittance is seen to increase, which indicates that when the desired effect is reached, the smoke production goes down. The results from the test with Halon 1301, as shown in Figure 24 a), show that this agent produces more smoke than the other agents tested, and at a REMP value rather close to extinction, as well. For the C_6F-ketone, no such conclusion can be drawn since no experiment close to extinction was performed.

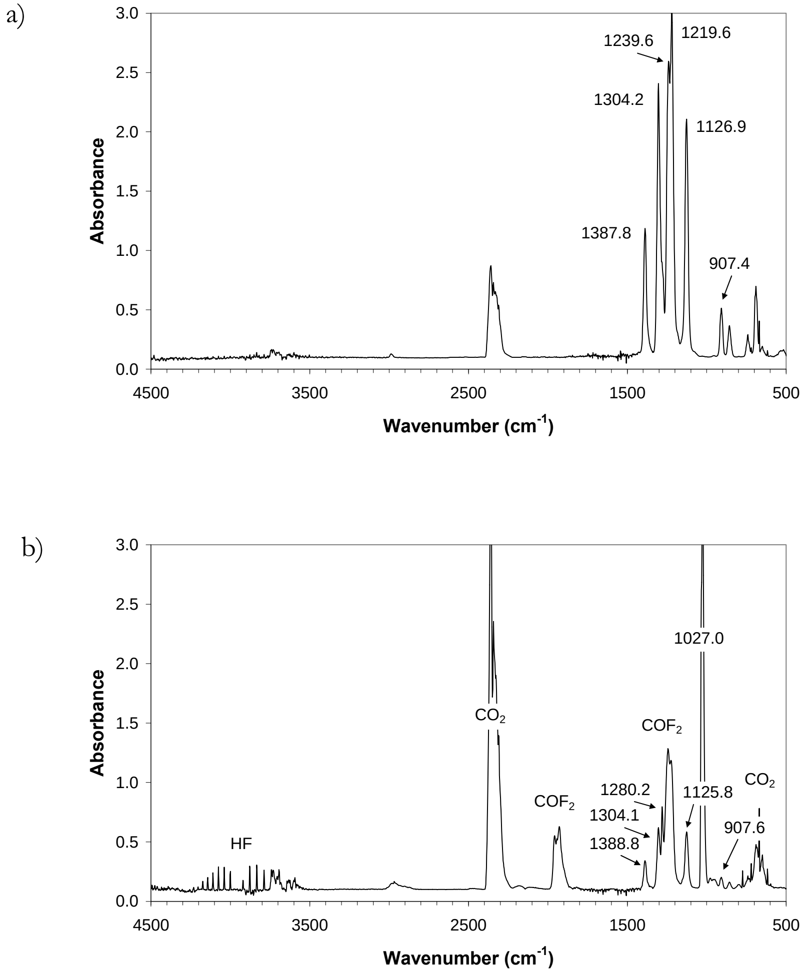


Figure 22. FTIR spectra from: a) approx. 640 ppm HFC 227ea mixed in air, b) combustion test with 91 %-REMP HFC 227ea.

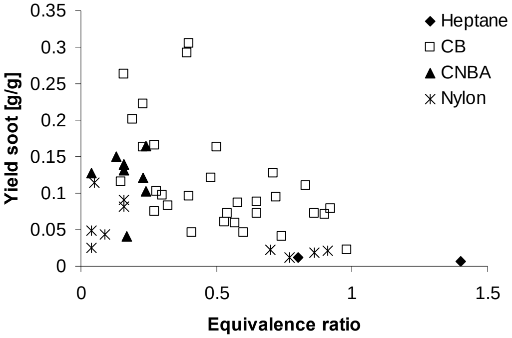
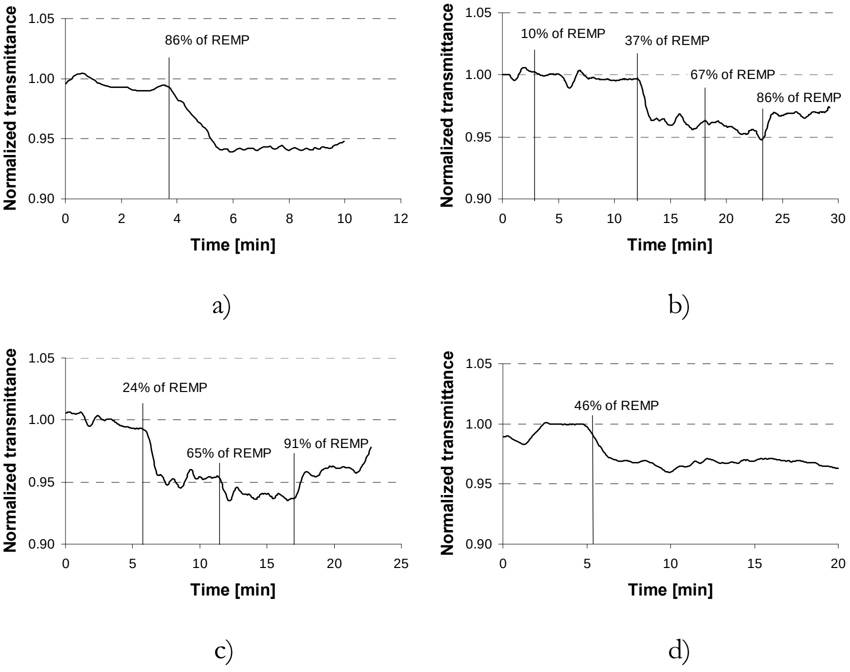


Figure 23. Yield of soot as a function of the equivalence ratio in experiments with heptane, chlorobenzene, CNBA and Nylon 6,6 in the 1/3 scale room.



a) b)

c) d)

Figure 24. Normalised transmittance of the combustion gases as a function of time, a) test 2 with Halon 1301, b) test 1 with HFC 125, c) test 2 with HFC 227 ea, d) test 3 with C_6F-ketone.

5.2 Production of nitrogen oxides and HCN

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" which was postulated by Y. B. Zeldovich in 1946 [66, 52] and "prompt or Fenimore NO", put forward by C. P. Fenimore in 1978 [67, 68]. The former is favoured by very high flame temperatures, >1700 K which are less likely during uncontrolled combustion. Stoichiometric and fuel-controlled combustion can also favour the Zeldovich mechanism. The reaction scheme for the thermal route for formation of NO_x is given in Figure 25. Since this mechanism was postulated, one more step is often included, Figure 26, and this set of three steps is referred to as the extended Zeldovich mechanism [69]. At these high temperatures, molecular nitrogen and oxygen can dissociate into their atomic states and they can then take part in the series of reactions given in Figures 25 and 26. Normally there is a very high surplus of oxygen in a flame (5-10 times the stoichiometric concentration) and the residence time is short. These factors make the thermal route to NO_x less likely under fire conditions.

$$\mathbf{N_2 + O \longrightarrow NO + N}$$

$$\mathbf{N + O_2 \longrightarrow NO + O}$$

Figure 25. Reaction scheme for the thermal NO_x formation [66].

$$\mathbf{N + OH \longrightarrow NO + H}$$

Figure 26. The third step included in the extended thermal or Zeldovich mechanism [69].

The prompt or Fenimore mechanism is more complicated and is the result of the reaction between a CH radical and nitrogen from the surrounding air forming HCN which then reacts with nitrogen to form NO. The originally proposed reaction schemes for the production of HCN are presented in Figure 27. This mechanism is favoured in rich flames. It has been debated that these reactions are not the only ones responsible for the production of prompt NO. Many attempts have been made to find the complete set of reactions. For example, Bowman [70] suggests the scheme in Figure 28 for possible routes to the production of prompt NO from HCN.

$$CH + N_2 \rightarrow HCN + N$$

$$CH_2 + N_2 \rightarrow HCN + NH$$

Figure 27. Schematic presentation of the HCN formation according to Fennimore [67, 68].

Under fuel-controlled combustion an additional mechanism is possible, as postulated by Wolfrum [71]. It is a reaction between nitrogen in the air and an oxygen atom in the presence of a third molecule, Figure 29. The N_2O can further react with oxygen to produce NO; this was suggested by Malte and Pratt in 1974 [72] according to the scheme in Figure 30. The latter reaction is often omitted as it often gives a much smaller contribution to the overall production of nitrogen oxides. However there are situations in ventilation-controlled conditions when the production of prompt NO is limited and the production of Zeldovich NO is restricted due to low temperatures. In these circumstances, the reactions in Figures 29 and 30 are the main paths to the production of nitrogen oxides.

$$HCN + O \rightarrow NCO + H$$

$$NCO + H \rightarrow NH + CO$$

$$NH + (H, OH) \rightarrow N + (H_2, H_2O)$$

$$N + OH \rightarrow NO + H$$

$$N + O_2 \rightarrow NO + O$$

Figure 28. Production of prompt NO from HCN suggested by Bowman [70].

$$N_2 + O + M \rightarrow N_2O + M$$

Figure 29. Production of N_2O from N_2 and O involving an extra molecule M [71].

$$N_2O + O \longrightarrow NO + NO$$

Figure 30. Presentation of the formation of NO from N_2O and O [72].

Fuel-bound-nitrogen presents a fourth possible reaction route for production of NO. This path is possible in the combustion of nitrogen-containing carbon compounds. It has been found that the conversion of fuel-bound-nitrogen to NO is strongly dependent on the local combustion environment and, only to a small degree, on the original fuel molecule. When these nitrogen-containing substances are heated, they are decomposed into low-molecular-weight compounds containing nitrogen such as NH_3, NH_2, NH, HCN or CN. A scheme for the formation of prompt NO including-fuel-bound nitrogen is presented in Figure 31.

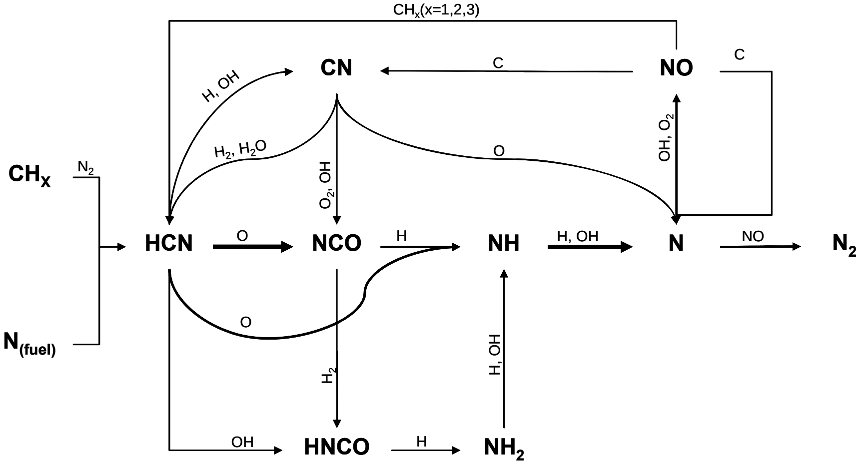


Figure 31. Reaction scheme for the transformation of fuel-bound-nitrogen to NO_x and HCN [70].

Glarbourg et al. [73] have further evaluated possible reactions for the production of nitrogen oxides when hydrocarbons are present. They suggested that under fuel-rich, ventilation-controlled burning, the set of three reactions, presented in Figure 32 below, is rate-controlling for the conversions between HCN and NO.

$$C + NO \leftrightarrow CN + O$$

$$CH + NO \leftrightarrow HCN + O$$

$$CH_2 + NO \leftrightarrow HCNO + H \leftrightarrow HCN + OH$$

Figure 32. Possible reactions for production of nitrogen oxides in the presence of hydrocarbons [73].

They also present a fourth reaction which can contribute to the production of HCN [73], Figure 33.

$$CH_3 + N \leftrightarrow HCN + 2H$$

Figure 33. Reaction for production of HCN in the presence of hydrocarbons [73].

The experiments in the TOXFIRE project included substances containing nitrogen. The production of NO_x in these experiments is illustrated in Figure 34, where the production of nitrogen oxides is presented as yields for three nitrogen containing substances, Nylon 6,6, TMTM and CNBA.

The thermal mechanism is favoured at very high flame temperature, which is 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 also made a minor contribution to the overall NO_x yields found in the TOXFIRE experiments. Thus the major part of the NO_x emissions will be due to the nitrogen in the fuel. The production of nitrogen oxides follows the same pattern for all substances investigated. A decrease in NO_x with increasing equivalence ratio 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.

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 result in different nitrogen oxides, N_2 and CO or CO_2. Much work has been presented on the issue of HCN formation during combustion and also on the oxidation of HCN into nitrogen oxides. For instance, Dagaut et al. presented an extensive compilation on the subject [74]. In experiments with nylon and TMTM, an increase in the HCN yield with increasing equivalence ratio was found, but for the chlorine-containing CNBA, the behaviour was the opposite. Results are presented in Figure 35 for experiments with nylon, TMTM and CNBA.

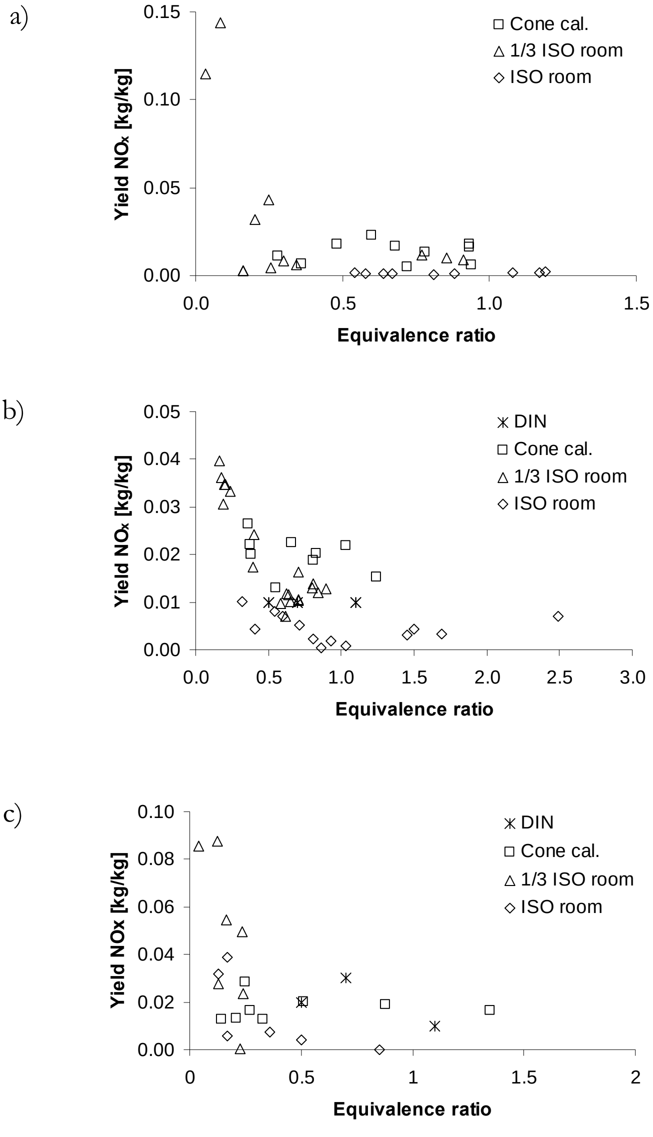


Figure 34. The yield of nitrogen oxides is presented as a function of the equivalence ratio for experiments with a) Nylon 6,6, b) TMTM, c) CNBA.

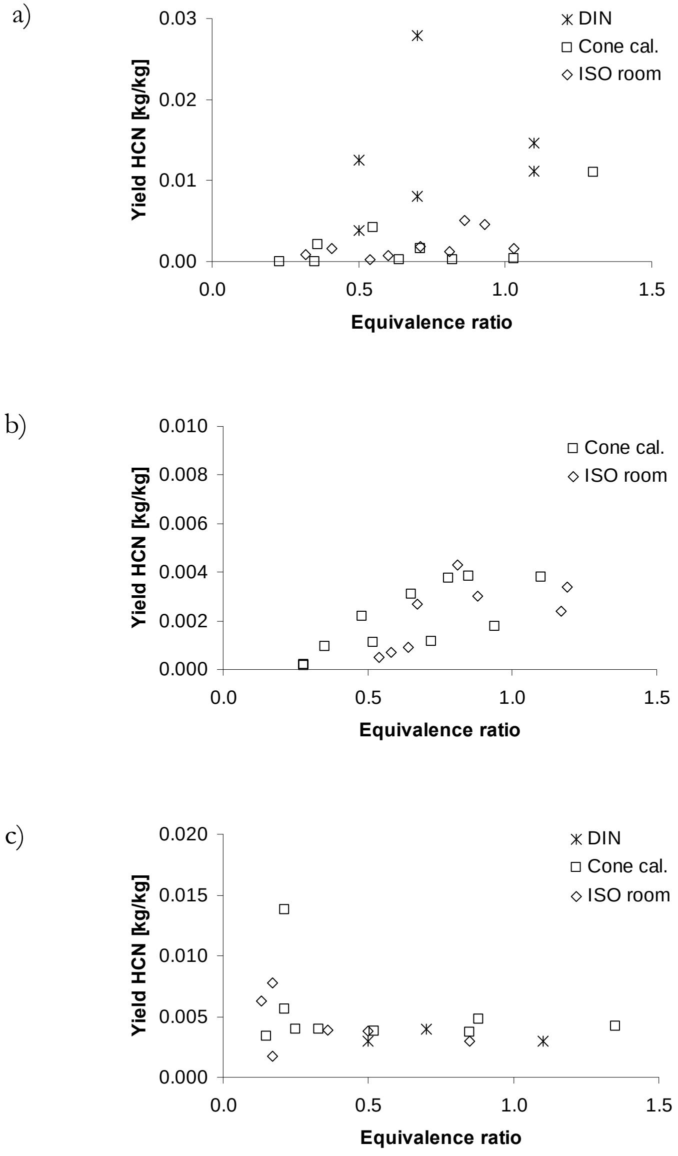


Figure 35. The yield of HCN is presented as a function of equivalence ratio for experiments with a) Nylon 6,6, b) TMTM, and c) CNBA.

The results from the TOXFIRE experiments are supported by experiments by Glarborg et al. [73]. They found that when nitrogen-containing substances were added to a hydrocarbon flame, 60-100 % of the added nitrogen was converted to NO_x in fuel-controlled conditions. In ventilation-controlled conditions, the results were different. The emission of NO_x was much lower and approached zero when the equivalence ratio was around 1.6. This behaviour was also seen in the TOXFIRE experiments. An explanation of why the production of HCN from CNBA is quite different from the others has not been found.

The chemicals in the halon replacement project were all non-nitrogen containing hence neither NO_x nor HCN was measured during those experiments.

5.3 Production of HCl

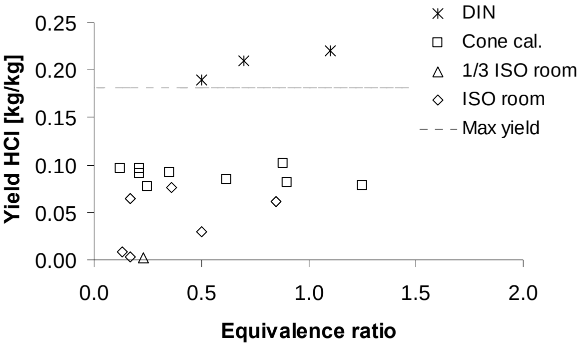
In connection with combustion of waste and chlorine-containing substances such as polymers in other situations, the production of HCl is a source of concern since it is highly corrosive and can cause damage to property even when it is present in small amounts. It is also highly irritating and toxic to humans. 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. Even at low temperatures (200°C), HCl is produced from PVC and increasing temperature does not seem to increase the production of HCl [75]. Other chlorine-containing substances can also be expected to release HCl, but the temperature at which HCl is released and the extent to which chlorine is given off as HCl may vary depending on the chemical structure of the substances involved.

Two chlorine-containing substances, CB and CNBA, were included in the TOXFIRE project and they behaved differently from PVC. For CB, a high temperature, i.e. one greater than 900°C, is needed to cause high level of HCl release. Such high temperatures are 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, in principle, to be independent of the equivalence ratio. This can be seen in the graphs in Figure 36.

Results from experiments with CB can be found in the literature. The purpose of such studies is mainly to see what compounds are produced from the thermal degradation of CB at high temperatures. The main objective is then to find what substances can be expected when chlorine-containing waste is combusted in an incinerator. CB is chosen since it is the simplest of the cyclic aromatic compounds containing chlorine. Detailed mechanisms for the destruction of CB are presented by Fadli et al. [76] and Higgins et al. [77]. Studies of how HCl is released from PVC at relatively low temperatures, i.e.

60-120°C, over long periods of time can also be found [78]. It is however difficult to find information on the flaming combustion of CB and other chlorine containing compounds.

a)



b)

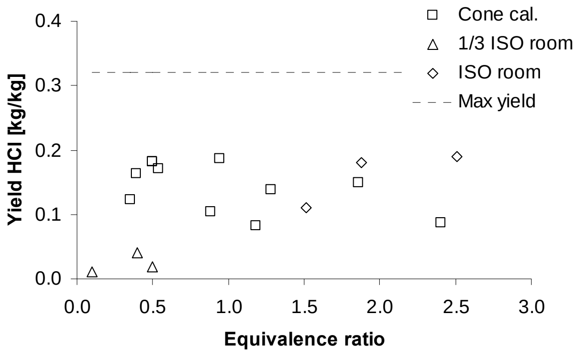


Figure 36. The yield of HCl is presented as a function of the equivalence ratio for experiments with a) CNBA and b) CB. The dashed line in both diagrams represents the maximal theoretical yield of HCl.

One problem which is well known is that when present in the combustion gases from a fire in an enclosure the HCl concentration decreases over time. This is due to the fact that HCl adheres to the surrounding surfaces. Efforts have been made to model this behaviour. In 1989 Galloway and Hirschler [79] presented a model to be incorporated into zone models for the deposition of HCl. This concept was further developed by Wang et al. [80] who implemented a model for the CFD model Smartfire [81].

When chlorine-containing substances are taking part in a fire or are combusted, there is always concern for the possible production of dioxins and chemically similar substances. This problem was also addressed in the TOXFIRE project. However, no sampling for dioxin analysis was made in the 1/3 scale ISO room test. Since the part of the project carried out at Lund focused on the medium scale, no thorough presentation of the results is made here. The results are presented in detail in the paper by Vikelsøe and Johansen [23].

No chlorine-containing substances were incorporated in the halon replacement project.

5.4 Production of fluorine-containing substances

Organic compounds containing the halogen, fluorine, can be expected to produce breakdown products such as hydrogen fluoride, HF and carbonyl fluoride, COF_2, as well as larger fragments of the parent molecule when they are exposed to high temperatures. Fluorine-containing substances are to be found among the multitude of halon-replacement agents that have been developed since the ban on halons. In order to understand and predict the concentration of toxic species when introducing fire-suppressing agents into the combustion process, reaction kinetics need to be developed and applied in combustion models. A number of experimental and theoretical studies on reaction kinetics for fire-extinguishing agents can be found in the literature. Most existing studies focus on the fire-retarding and extinguishing characteristics of the agents but a few focuses on the modelling of the combustion process. However, some experimental studies on thermal decomposition of mixtures of fuel and extinguishing agents have been found [82, 83, 84, 85]. Furthermore Burgess et al. [86] present a comprehensive chemical kinetic mechanism for the destruction and flame suppression capability of fluorinated hydrocarbons with one or two carbon atoms. Reaction classes are described beginning with C_1 fluorinated hydrocarbons and followed by C_2 hydrocarbons. In the hydrocarbon structure of these compounds, one or more hydrogen atoms are replaced by fluorine.

Since HF is a toxic and corrosive substance, it is interesting to study how it can be formed in reactions between fluorine-containing substances, such as extinguishing agents, and other combustion products readily available in the combustion gases from a fire. In Tables 9 and 10, a number of reaction paths for the formation of HF are presented from the work by Burgess et al. [86].

Table 9. Formation of HF from H/F/O.

$H_2 + F = H + HF$

$OH + F = O + HF$

$HO_2 + F = O_2 + HF$

$H_2O + F = OH + HF$

$H_2O_2 + F = HO_2 + HF$

Table 10. Main paths for formation of HF from C_1-fluorohydrocarbons.

F atom abstraction by H where $x \in \{0,3\}$

$CH_xF_{4-x} + H = CH_xF_{3-x} + HF$

H abstraction of fluoromethanes from HCO by fluoromethyls where $x \in \{0,2\}$

$HCO + CH_xF_{3-x} = CH_xF_{2-x}CO + HF$

Oxidation of fluoromethyls by OH $x \in \{0,2\}$

$CH_xF_{3-x} + OH = CH_xF_{2-x}O + HF$

Oxidation of the fluoromethylenes CHF and CF_2 *by* H_2O *and OH*

$CHF + H_2O = CH_2O + HF$

$CF_2 + H_2O = CHF{:}O + HF$

$CHF + OH = HCO + HF$

$CF_2 + OH = CF{:}O + HF$

Destruction of the flurometholenes CHF and CF_2 *by H and* CH_2O

$CHF + H = CH + HF$

$CF_2 + H = CF + HF$

$CHF + CH_2O = CH_2CO + HF$

$CF_2 + CH_2O = CHFCO + HF$

Burgess et al. also present reaction schemes for production of HF from fluorohydrocarbons with two carbon atoms. This mechanism includes more than 100 reactions involving HF. A complete list of these reactions can be found in [86].

Carbonyl fluoride, COF_2, is another possible, highly toxic, product when fluorinated hydrocarbons are involved in a combustion process. Reaction paths involving COF_2 are also presented by Burgess et al. [86]. Reactions with fluorinated hydrocarbons with one carbon atom are presented in Table 11. For reactions with substances containing more carbon atoms, the reader is referred to [86]. In reactions where COF_2 reacts further, it most frequently decomposes to give HF.

Table 11. Reactions involving COF_2 [86].

CHF_2	+	O_2	=	COF_2	+	O	+	H
CHF_2	+	O	=	COF_2	+	H		
CF_3	+	O	=	COF_2	+	F		
CF_3	+	OH	=	COF_2	+	HF		
CHF_2	+	HO_2	=	COF_2	+	OH	+	H
CF_3O	+	H	=	COF_2	+	HF		
CF_3O	+	H_2	=	COF_2	+	HF	+	H
CF_3O	+	H_2O	=	COF_2	+	HF	+	OH
CF_3O	+	CH_4	=	COF_2	+	HF	+	CH_3
CF_3O	+	C_2H_6	=	COF_2	+	HF	+	C_2H_5
CF_3O	+	C_2H_4	=	COF_2	+	HF	+	C_2H_3
CF_3O	+	C_2H_2	=	COF_2	+	CH_2CF		
CF_3O	+	CH_2O	=	COF_2	+	HF	+	HCO
CF_3O	+	HCO	=	COF_2	+	HF	+	CO
CF_2	+	O_2	=	COF_2	+	O		
CF_2	+	OH	=	COF_2	+	H		
CF_2	+	HO_2	=	COF_2	+	OH		
CFO	+	F	=	COF_2				
COF_2	+	H	=	CFO	+	HF		
CF_2O	+	H_2O	=	CO_2	+	2HF		
COF_2	+	OH	=	CO_2	+	F	+	HF
CF_3O	+	M	=	CF_2O	+	F		

A number of studies of reactions between simple fuels (e.g. hydrogen and methane) and fluorinated extinguishing agents can be found. Hynes et al. [83] studied the composition of combustion gases when C_3F_7H, HFC 227ea, were introduced into a lean hydrogen-air flame. They present reaction schemes for the decomposition of C_3F_7H and for the production of COF_2. Further work by Hynes and co-workers was published in 1999 [87]. They then presented a mechanism for the pyrolysis of C_3F_7H, but the oxidation paths were not studied. Hynes et al. also presented a study on a hydrogen-ethane-air flame at atmospheric pressure and at lean conditions. In this study the concentrations of combustion gases above the flame was measured and compared to computed levels. A mechanism for the formation of COF_2 is also presented [88]. The concentrations of the combustion gases were measured at 2 mm and 15 mm above the burner.

Linteris presents a mechanism for the production of HF and COF_2 from the decomposition of CF_3H [84]. The mechanism is based on experiments performed by Vandooren et al. [89]. Vandooren et al. described the following chain of reactions, Figure 37, for the production and destruction of COF_2. They found the rate for the last reaction to be very sensitive to temperature.

$$\mathbf{CF_3H + H \longrightarrow CF_3 + H_2}$$

$$\mathbf{CF_3 + OH \longrightarrow COF_2 + HF}$$

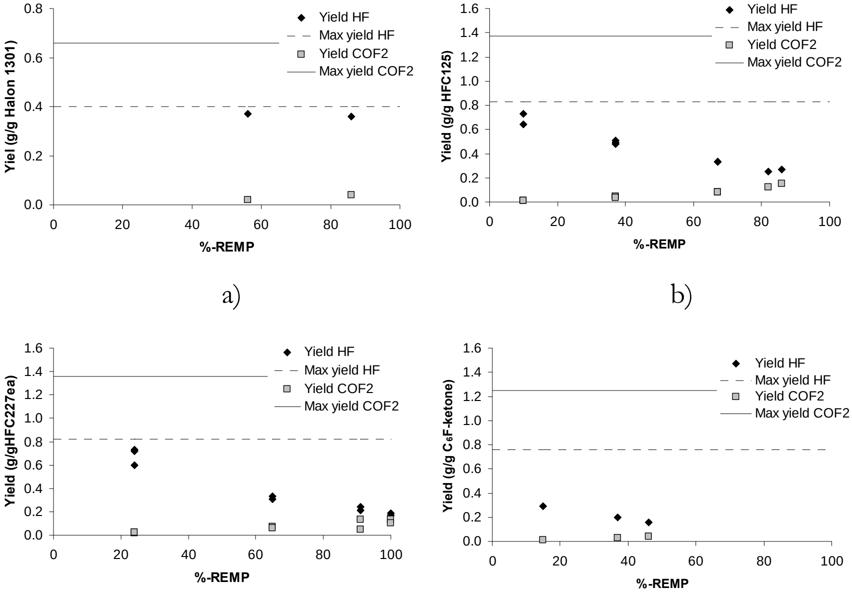
$$\mathbf{COF_2 + H \longrightarrow CFO + HF}$$

Figure 37. Possible reaction chain for the production and destruction of COF_2 [89].

Studies by Babushok and Tsang, [90], show that HF and COF_2 can be formed when fluorinated hydrocarbons are introduced into a burning fuel. Whether the fuel is H_2, CH_4 or a more complex hydrocarbon seems to be of minor importance. Their studies contain conclusions on how HF and COF_2 can be formed but do not predict the amount that can be expected when a specific fluorinated hydrocarbon is introduced into a flame.

In the halon-replacement project, four fluorine-containing extinguishing agents were added to a propane flame and the concentrations of HF and COF_2 were measured with FTIR. The yields of HF and COF_2 in the tests are shown in Figure 38. For example, in Figure 38 c), the results from all tests conducted with HFC 227ea are plotted versus the relative application rate of the extinguishing agent. The yields are expressed as the quotient of the production rate of the halogenated compound and the application rate of HFC 227ea. The relative application rate of HFC 227ea on the x-axis is expressed as the application rate relative to the REMP value. The REMP value corresponds to the application rate for extinction (100 %).

The data in Figure 38 are presented as yields, i.e. mass of combustion product produced per mass of extinguishing agent applied. The maximum theoretical yields for HF and COF_2 are indicated in the diagrams as reference. It is clear from Figure 38 that both HF and COF_2 are produced from all four extinguishing agents. The yield of HF decreases for HFC 125, HFC 227ea and $C_6F_{12}O$ with increasing application rate of the extinguishing agent. The yield of HF is very high for both HFC 125 and HFC 227ea, about 0.7 g/g at low relative application rates. The yield of HF from $C_6F_{12}O$ is significantly lower at low relative application rates. No results are available for high relative application rates for $C_6F_{12}O$. The yield of HF from Halon 1301 is rather constant at the two relative application rates investigated, i.e. about 0.4 g/g and close to the maximal theoretical yield. On the other hand, the yield of COF_2 increases with increasing application rate for all the extinguishing agents. It is probable that at low relative application rates, the organic extinguishing agent is largely consumed and fluorine is effectively transferred to HF. At higher relative application rates, where the extinction effect becomes more evident, the consumption of the extinguishing agent is less effective and the formation of COF_2 is favoured over HF.

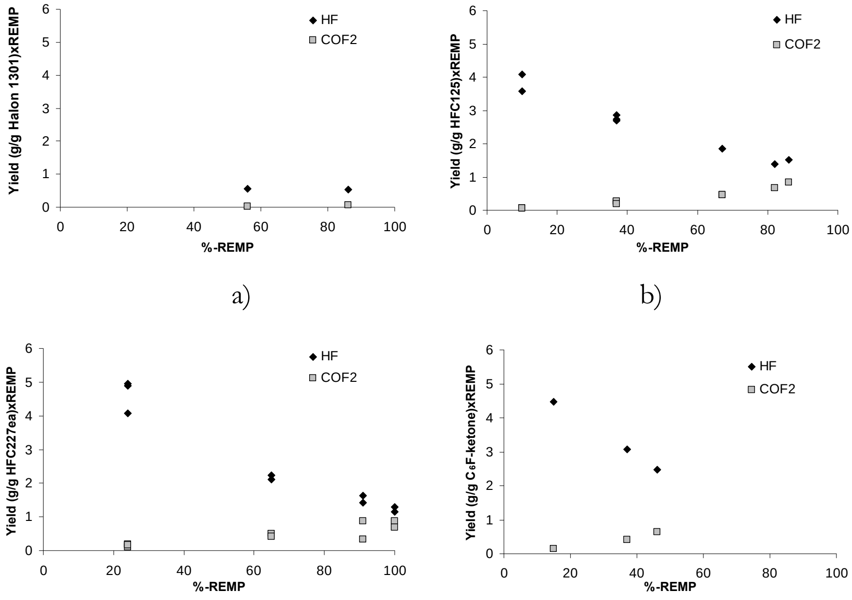


a) b)

c) d)

Figure 38. Yields of halogen containing combustion products from the tests with: a) Halon 1301, b) HFC 125, c) HFC 227ea and d) C_6F-ketone.

The data in Figure 38 thus give no direct information on the amounts of combustion products produced in fires when comparing the four tested extinguishing agents. In a full-scale evaluation of halon-replacement agents, Kim and Su [91] report that the concentration of HF in the test compartment was 5-10 times higher for halon-replacement agents than for Halon 1301. These results are also supported by those presented by Holmstedt et al. [92]. The same trend is found in the results presented in Figure 38. In order to make a comparison possible, the yields for each extinguishing agent were multiplied by their respective REMP-value. These normalized yield data are presented in Figure 39. The results show that, at lower relative application rates, the absolute production of HF from $C_6F_{12}O$ is comparable to that from HFC 227ea and HFC 125. This means that even though the yield of HF from $C_6F_{12}O$ is lower, the absolute production is still large due to the high REMP-value. Figure 39 further shows that the absolute production of HF from Halon 1301 is significantly lower compared to the newer alternative extinguishing agents.

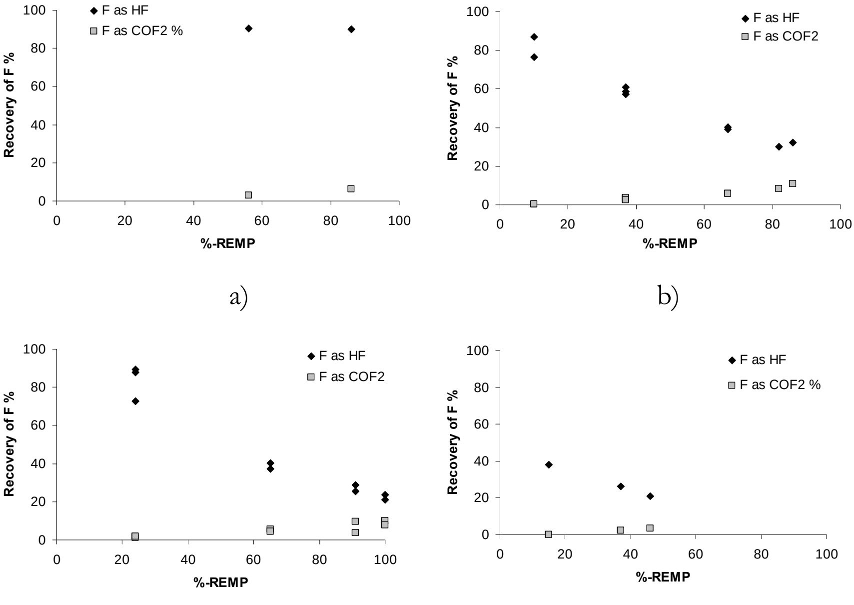


a) b)

b) d)

Figure 39. Yields of halogen containing combustion products, normalized against the REMP value, from the tests with: a) Halon 1301 - REMP = 1.5, b) HFC 125 - REMP = 5.6, c) HFC 227ea - REMP = 6.8 and d) C_6F-ketone - REMP = 15.4.

The recovery of fluorine as HF and COF_2 has been calculated for the extinguishing agents and is presented in Figure 40. The main fraction of fluorine ends up as HF for HFC125 and HFC227ea at lower relative application rates. As the extinguishing concentrations are approached, the fraction recovered as COF_2 increases, but the total recovery of fluorine, including HF, is below 40 % at a 90 % relative application rate. The recovery of fluorine as HF and COF_2 for C_6F-ketone is lower compared to HFC 125 and HFC 227ea. There is a clear difference in the recovery for Halon 1301 where an almost total recovery as HF or COF_2 is found for fluorine. Halon 1301 contains bromine also, which, to a large extent, is recovered as HBr.



a)

b)

c)

d)

Figure 40. Recoveries of fluorine (and bromine in one case) from the tests with: a) Halon 1301, b) HFC 125, c) HFC 227ea and d) C_6F-ketone.

5.5 Production of SO_2

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 project. It was found that the sulphur dioxide yield was high at equivalence ratios less than 1, and decreased for equivalence ratios greater than 1, Figure 41. Sulphur compounds other 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 [9].

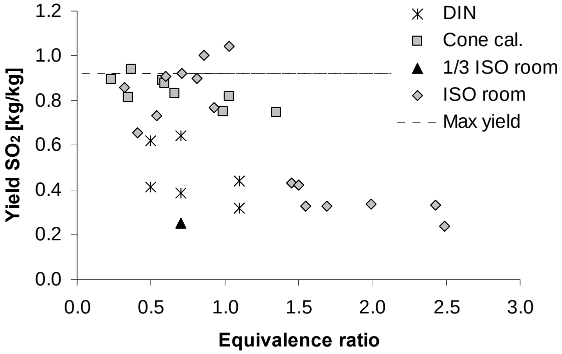


Figure 41. Yields of SO_2 from experiments with TMTM in different scales in the TOXFIRE project.

In the project with halon-replacement agents no substance containing sulphur was included.

6 Fire hazard analysis

Fires pose a potential threat to people, property and to the environment. A hazard analysis with respect to fire demands large amounts of input data regardless of the angle of approach. Here, the emphasis is on acute hazards for humans, specifically toxic gases. The results presented can, naturally, also be used for other purposes. There are a variety of reasons why people die or are injured in fire accidents. Toxic gases and soot in the smoke coming from the fire and injuries caused by heat are the factors most frequently mentioned. Various approaches have been used over the years for finding representative data for these variables as input in hazard analysis.

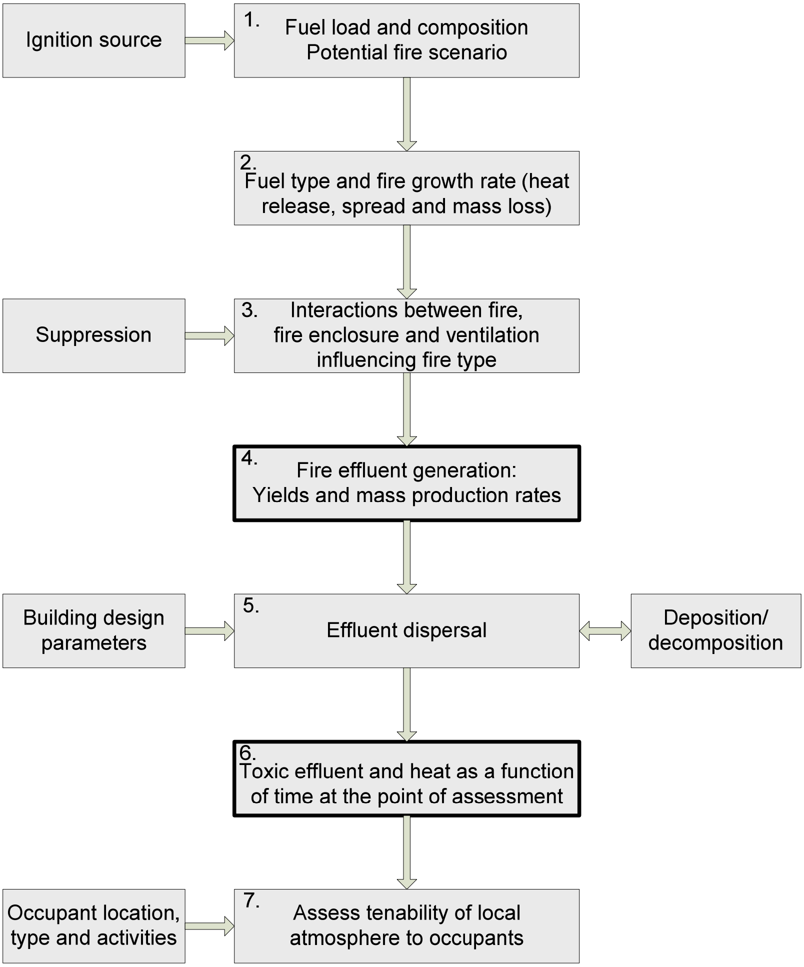


Figure 42. Elements of a fire hazard analysis [93].

In order to make good estimates of the effects of fire gases on humans for use in hazard analysis and as input to hazard assessments, good and reliable data are of utmost importance. In most cases these data are based on experimental results although the specific figures can come from calculations. Guidelines for the production of such data have been prepared by organisations such as ISO, the International Organization for Standardization. Specifically ISO 19706, "Guidelines for assessing the fire threat to people" [93] and ISO/TS 13571, "Life-threatening components of fire – Guidelines for the estimation of time available for escape using fire data" [94] should be mentioned.

The elements of fire hazard analysis according to ISO 19706 [93] are shown in Figure 42. Seven different levels of influencing elements can be discerned. Levels 4 and 6 are of main interest here but also levels 1 and 2 are involved since a number of different fire scenarios have been used in the study of production of combustion gases.

6.1 Influence of fire gases

The influence of fire gases result in incapacitation of humans and this can prevent people from escaping an ongoing fire. The incapacitation can be a result of:

- inhalation of asphyxiant gases
- exposure to irritating gases
- reduction of visibility due to smoke
- injury due to radiation from hot fire gases

Combinations of these effects, i.e. synergistic effects, are also possible and highly relevant, although they are difficult to incorporate in a hazard analysis. The main focus here is on the toxicity and the consequences of the presence of soot in the fire gases.

6.1.1 Asphyxiant fire products

Asphyxiant gases are gases that cause a decrease in the oxygen that is available for the necessary processes in the body. This affects the nervous system and can result in unconsciousness and ultimately death. The effect of such substances is related to accumulated doses, and is therefore dependent both on the concentration and on the exposure time. This results in an augmented effect with an increasing dose. The most studied gases in this group are carbon monoxide, CO, and hydrogen cyanide, HCN. Also low concentrations of oxygen, O_2 (less than 15 %) and very high concentrations of carbon dioxide, CO_2 (higher than 5 %) [95] can have narcotic effects.

Limiting concentrations for the most common asphyxiant gases are given in Table 12. The Occupational Exposure Limit values (OEL) are the concentrations that are deemed acceptable in a working environment by the Swedish Work Environment Authority. The Immediately Dangerous to Life and Health (IDLH) concentrations are laid down by the American National Institute for Occupational Safety and Health (NIOSH).

Table 12. Limiting values for asphyxiant gases.

Substance	**OEL[1)]** **[96]**	**IDLH[2)]** **[97]**
CO	100 ppm	1 200 ppm
CO_2	1 %	4 %
HCN	4.5 ppm	50 ppm

[1)] Swedish occupational exposure limits, for one working day, 8 h.

[2)] Immediately dangerous to life or health concentrations (NIOSH), normally based on an exposure of 30 min.

There is also a need for other types of limiting concentrations. ISO has presented limits for tenability for asphyxiant gases given as time to incapacitation and to death after exposure for 5 min and 30 min, Table 13 [98].

Table 13. Tenability limits for asphyxiant gases according to ISO/TR 9122-1 [98].

Substance	**5 min**		**30 min**	
	Incapacitation	**Death**	**Incapacitation**	**Death**
CO	6000 – 8000 ppm	12000 – 16000 ppm	1400 – 1700 ppm	2500 – 4000 ppm
HCN	150 – 200 ppm	250 – 400 ppm	90 – 120 ppm	170 – 230 ppm
O_2	10 – 13 %	<5%	<12 %	6 – 7 %
CO_2	7 – 8 %	>10 %	6 – 7 %	> 9 %

6.1.2 Irritant fire products

Combustion products can cause irritation to the sensory/upper respiratory system as well as to the pulmonary system. The irritant effect on the sensory system is immediate and dependant on concentration rather than on dose.

Effects on the pulmonary system can be delayed thus becoming more dependent on dose than on concentration. Limiting values and tenability for some inorganic irritants occurring in fire gases are presented in Table 14.

Table 14. Limiting values and tenability limits for irritants.

Substance	**OEL[1] (ppm) [96]**	**IDLH [2] (ppm) [97]**	**Severe sensory irritancy in humans (ppm) [10]**
HBr	2	30	100
HCl	5	50	100
HF	2	30	120
NO	50	100	-
NO_2	5	20	80
SO_2	5	100	50-100

[1] Swedish occupational exposure limits, for one working day, 8 h.

[2] Immediately dangerous to life or health concentrations (NIOSH), normally based on an exposure of 30 min.

6.1.3 Reduction of visibility

A fire can cause a substantial decrease in visibility due to the presence of soot particles in the combustion gases. Since smoke contains gases, particles of different sizes and geometries as well as droplets, smoke is a far more inhomogeneous mixture than combustion gases which have passed through filters for removal of soot and condensates. Molecules of irritating substances present in the combustion gases can adhere to soot particles and hence cause irritation to humans. Toxic products of other types can also be coupled to the soot particles but their main effect is to reduce visibility and thus make evacuation more difficult. The synergetic effects of smoke particles and various combustion gases among the combustion products must not be overlooked but they are nevertheless problematic to consider in a hazard analysis.

Since smoke can have varying effects on humans, it is difficult to give specific limits for tenability and levels of irritation. Experiments on visibility through fire smoke were made in Japan in the 1970's and are presented by Jin [99, 100]. It was found that the complex properties of fire smoke make it difficult to find simple relations between visibility and the extinction coefficient. Compilation of results from a number of experiments shows a great scatter. Some guidance can however be obtained from the results. For a visibility of 10 meters an extinction coefficient of 0.5 m^{-1} (ln scale) was found for irritant smoke, and for non-irritant smoke, an extinction coefficient of 0.7 m^{-1} (ln scale) was obtained for the same level of visibility. These results are from experiments in a corridor filled with smoke. The irritant smoke was produced by burning wood cribs and the non-irritant smoke came from a kerosene fire. The objects on which the visibility was measured were illuminated fire-exit signs. In order to estimate the possibilities for people to evacuate from a smoky environment the walking speed was also measured. For the same conditions as given above the walking speed in non-irritant smoke was found to be 0.7 m/s and for irritant smoke it was 0.3 m/s. The latter is of the same magnitude as walking speed in complete darkness. Experiments of the same type as reported by Jin have been performed by Frantzich and Nilsson [101]. Results from the latter series of experiments confirmed the results from Jin that there is a large scatter in the data probably due to both variations in the composition of the smoke and to variations in the sensitivity among the participants in the experiments.

6.2 Human exposure models

In order to estimate the influence a fire can have on exposed humans, models are needed since it is rarely possible to find data from real life situations. The models are often based on results from tests of materials, substances or components in selected bench-scale tests. Tests at larger scales are also done, but not as frequent as bench- or small-scale tests. These tests normally give a direct measurement of the studied variable as a function of time. For measurement of toxicity, the standard output variable is the toxic potency, given as LC_{50}, which is the concentration that is lethal to 50 % of the population exposed to this concentration for a specified period of time, typically 5 or 30 minutes. Longer periods of time can also bee used when effects other than acute effects are also being studied. Examples of concentrations that are immediately dangerous to life or health, are given in Table 14. These are based on LC_{50} values from animal exposure and here, the time of exposure has been set to 30 min [102]. This period was chosen so that the affected person has a possibility to get out of the exposed area.

Combustion gases rarely consist of one single combustion product, but rather, they comprise a mixture of a varying number of components. A technique of adding toxic potency for interesting products in the studied combustion gases has been adopted by the research community. It is called the Fractional Effective Dose, FED [103]. In short it can be written as:

$$FED = \sum_{i=1}^{n} \int_{0}^{t} \frac{C_i}{(Ct)_i} \cdot dt \qquad \text{Eq. 19}$$

This concept has been widely adopted and is incorporated into standards published by organisations such as ISO [104], ASTM, the American Society for Testing and Materials [105] and NFPA, the National Fire Protection Association [106].

The expression in Eq. 19 assumes that there is no interaction between the various components, and that their individual effects can be added linearly. It is known that synergistic effects occur but how they influence the overall effect of the smoke gases is not fully understood. For instance, the presence of one gas can increase the action of another [107, 108]. An example of such an effect is that high levels of CO_2 result in an increase in the effect of CO. Levin and co-workers presented a model, called the N-gas model, in which LC_{50} values determined for each specific and relevant component in the combustion gases are combined into a FED value, as in Eq. 20 below, [107, 109]. This method reduces the number of toxicity tests that must be performed.

$$\frac{m[CO]}{[CO_2]-b} + \frac{[HCN]}{LC_{50}HCN} + \frac{21-[O_2]}{21-LC_{50}O_2} + \frac{[HCl]}{LC_{50}HCl} + \frac{[HBr]}{LC_{50}HBr} = FED \qquad \text{Eq. 20}$$

The first term in Eq. 20 represents the influence of the CO_2 concentration on the effect from CO. The third term takes the effect of lowered O_2 concentration into account.

The FED value resulting from Eq. 20 can be used to determine the toxic potency for a specific substance or material, according to Eq. 21 where *m* is the mass of the combustion gases and *V* is the volume in which the gases are distributed. This gives a LC_{50} expressed as g/m^3 and is specific for the tested substance or material.

$$LC_{50} = \frac{m}{FED \cdot V} \qquad \text{Eq. 21}$$

Other approaches have also been introduced such as the use of probit functions, Eq. 22.

$$\Pr = a + b \cdot \ln(c^{n \cdot t}) \qquad \text{Eq. 22}$$

Pr represents the response expressed as a probability for a person to react in a specific way upon exposure to a certain toxic load, in terms of a dose of a given substance, c is the concentration and t is the duration of the exposure and a, b and n are constants specific for each substance and the type of effect that is studied [110, 111]. The effect can be death but it can also be various levels of irritation, illness and other effects. The use of probit functions is quite common in risk analysis where exposure to toxic gases is examined, but is not so widely spread in the fire research community in performing fire hazard analysis.

All combustion products can be included in what we normally refer to as smoke, i.e. gases, droplets and particles of varying sizes. From this, it follows that smoke influences people in a number of ways. As mentioned above, combustion products can be irritating and have choking effects. Smoke can also impair visibility and thus obstruct the possibilities of evacuation. In hazard analysis, this can be incorporated as a reduced walking speed, thus influencing the time to escape. Models for this purpose have been presented in previous reports, for instance, that of Purser [112].

7 Conclusions and future work

Fires involving substances that are toxic in themselves or can produce toxic combustion products are a potential threat to humans and to the surrounding environment. The toxic chemicals may be stored in warehouses, be under transport or even be used as extinguishing agents.

The case involving storage of toxic substances was investigated within the TOXFIRE project. A database containing data from selected warehouse fires was created. It contains data from fires that have actually occurred and can give a hint of what might happen when chemicals are on fire [113]. Within this project, some guiding principles for the design of such storage were also given [114].

Special groups of chemicals have been studied by researchers. Such groups are herbicides and pesticides, chemicals intended for weed and vermin control. Those chemicals are intended to be poisonous to herbs and undesirable insects and animals and therefore they are potentially poisonous to all living organisms. Possible results from fires in these substances have been reported in [115, 116, 117], to name a few. The results presented in these reports are built on the chemical structure of the studied compounds and on conventional methods of chemical breakdown and dispersion of substances in the surrounding air. Advice on suitable tactics for fire brigades when approaching a fire in a chemical warehouse has also been outlined [118]. Here the results are also built on calculations from assumed fire scenarios.

Other types of compounds or materials that have been investigated thoroughly are various polymers. Here the list of references could be enormous but it has been limited to a few of the more recent publications [119, 120, 121].

To make good fire hazard analyses or risk assessments, reliable input data are necessary since the result of the analysis or assessment can be no better than the data put into it or the models used in performing it. The work presented here is aimed at producing source characteristics for fire hazard analysis where substances of organic origin, containing hetero-atoms such as N, S, Cl and F are of interest. One aim is also to compare methods for producing these data.

Source characteristics for a number of different variables are needed as input to models for hazard analysis. Such characteristics may involve properties such as production of gases, particles and smoke, often given as yields, temperatures, rate of heat release and degree of ventilation. The latter three are often used to characterise the fire. They give a picture of the size of the fire and they also indicate what stage of the fire the data can represent. Data from experiments with the studied types of substances in a number of experimental set-ups have been collected and compared.

The task of performing fire experiments is complex and it is clear that producing reliable and useful data from such experiments is no simple matter. There are many sources of error that must be avoided.

To be able to use the data from fire experiments, it is sometimes necessary to study how the produced data compares to what happens in a real fire situation. It is then helpful to use some form of scaling procedure. A number of researchers, notably P. H. Thomas and J. G. Quintiere, for example, have presented comprehensive studies of scaling principles for fire situations [122, 123]. The principles of scaling of fire phenomena can be built on the differential equations for conservation of mass and energy and dimensionless numbers such as: Fr (Froude), Nu (Nusselt), Re (Reynold) and Pr (Prandtl) numbers. The construction of dimensionless groups of variables is also a central part of the scaling procedure. These dimensionless groups are often chosen to represent a characteristic length or velocity.

Scaling with dimensionless groups is useful for modelling key variables during controlled combustion but is not applicable for modelling production of minor combustion species. The main reason for this is that the production of combustion gases during a fire is influenced by factors such as turbulence, uncontrolled ventilation and residence time. Another fact is that the reaction kinetics in fires involving complex fuels is not yet well understood. There are models describing the formation of soot and NO_x for instance, during controlled combustion, but when the interest is on complex fuels, the only path available for modelling this is to start from the very simple molecules and try to build models for increasingly more complex fuels [124, 125].

The studies presented here are not examined using the type of scaling mentioned above. Rather normalized variables such as yields (the ratio of the production of a compound and the amount burnt of the studied substance) have been used to compare results from experiments at different scales. The ventilation conditions during a fire, expressed as equivalence ratio, are often used as a factor when comparing results from fire experiments. For example the production of CO and CO_2 from experiments with varying equivalence ratios has been compared. For fuels without hetero-atoms, good correlations were found between the equivalence ratio and the production of CO and CO_2 for the tested scales. The results could also be presented to agree with the correlations given by Tewarson [42]. For fuels with hetero-atoms, these correlations were found not to be applicable.

For the experiments with extinguishing agents, results from just one type of experiments are available so scaling studies could not be done. The results from measurements of CO and CO_2 show that for well-ventilated fires, the production of CO, as well as CO_2, is significantly increased when the agent is applied. This is an interesting observation, especially for CO, when the potential hazards with new extinguishing media are discussed, since not only must the toxicity of the burning substance, material or product and the toxicity of the combustion products from the initial fire be taken into consideration, but the toxicity of the added extinguishing media also, along with what happens to the combustion gases when the extinguishing agent is added. This is an area where more studies are needed, especially since new extinguishing agents are being put on the market in order to fulfil demands of good environmental qualities together with good extinguishing capabilities.

When organic substances are heated or combusted, they tend to break down into small and large fragments which can be potentially hazardous. Compounds with hetero-atoms, especially Cl, were found to be particularly insensitive upon heating. Such substances tested in the TOXFIRE project were found to give rather high survival fractions. A yield up to more than 5 % of the original substance was found in the combustion gases. If this is the case in a real fire, and the burning compound is a pesticide for instance, the effect on the environment could be enormous. This is also an area where there is still a lack of information and knowledge.

Substances containing Cl and the subsequent production of HCl upon heating, even at quite low temperatures, have long been of concern and many studies of PVC at elevated temperatures have been done, e.g. [78, 120]. For the substances in this study, CB and CNBA, the production of HCl seems to be largely independent of equivalence ratio and of the setup in which the experiment was performed.

In the experiments with extinguishing agents, traces of the used agent could also be found, but the main problem here is what happens to the large amounts of F available in the parent molecules. Most of the F occurs as HF which is an irritating toxic gas. Of far greater concern is the production of COF_2, carbonyl fluoride which is highly toxic at very low concentrations. Mechanisms for the formation of HF and COF_2 have been presented by a number of researchers [84, 86, 87]. The results from the studies presented here show that both HF and COF_2 are produced from all four extinguishing agents studied. It was also found that when the application rate of the agent is close to extinction of the flame, the formation of COF_2 is favoured over that of HF. This means that it is very important to have an application rate which is well adjusted to the fire it is designed to extinguish. Extinguishing systems are designed to be discharged at an early stage of the fire before the combustion comes into a ventilation controlled phase and the lay-out of the experiments was made to simulate this stage of the fire.

Nitrogen-containing substances are included in the study so the production of nitrogen oxides, NO_x, is also of interest. A number of pathways for the production of NO_x have been presented and accepted by the scientific community. For the substances and scenarios in the experiments studied here, it was assumed that the main production of NO_x came from N available in the fuel. This can be further emphasized by the fact that for substances with no N in the parent molecule, virtually no NO_x was detected.

For the substances containing N, the possible production of HCN is also of interest. It was found that the production of HCN for these substances increased with increasing equivalence ratio. This was, however, not the case for CNBA which contains Cl as well as N. This behaviour is still not fully understood.

One compound containing sulphur, S, was included in the TOXFIRE study. SO_2 was expected to be the main sulphur containing product in the combustion gases. This was confirmed by the gas analyses where it also was found that the yields of SO_2 were high at equivalence ratios less than 1 and then decreased. The choice of testing method seems to be of minor importance in investigating the yield of SO_2.

Although many results have been presented as being dependent on the ventilation conditions during the experiment, this is not the only dependence that should be taken into consideration. Temperature and residence time have also been found to have considerable influence on the final results.

Looking at the overall results, it can be concluded that it is possible to use small-scale experiments to get an indication of the combustion products that will be produced and also of the level of yields that can be expected in a fire involving chemicals.

References

1. NCO and SRV, “Bränders samhällsekonomiska kostnader – Resultat”, NCO 2008:6A, 2008 (in Swedish).

2. Marlair, G., Simonson, M., Gann, R. G., “Environmental concerns of fires: Facts, figures, questions and new challenges for the future”, Interflam, 325-337, 2004.

3. Smith-Hansen, L., “STEP – Combustion of chemical substances and the impact on the environment of the fire products, Final report”, Risö-R-764, 1994.

4. Petersen, K. E., Markert, F., “Assessment of fires in chemical warehouses – An overview of the TOXFIRE project”, Risø-R-932, 1999.

5. Haahr Jørgensen, K., Smith-Hansen, L., “TOXFIRE – Flash pyrolysis and DIN 53436 experiments”, Risø National Laboratory, Roskilde, Denmark, Risø-R-765, 1995.

6. Markert, F., “TOXFIRE: Results for CNBA and TMTM combustion in DIN furnace”, Risø National Laboratory, Roskilde, Denmark, Risø-R-883, 1996.

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

8. 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 1996.

9. Andersson, B., Babrauskas, V., Holmstedt, G., Särdqvist, S., Winter, G., “Simulated fires in substances of pesticide type”, Department of Fire Safety Engineering, Lund University, ISRN: LUTVDG/TVBB-3087-SE, Lund 1999.

10. Purser, D. A., “Toxicity assessment of combustion products” In the SFPE Handbook of Fire Protection Engineering, 2nd ed., (Di Nenno, P. J. Ed.) 2:83-146, NFPA, Quincy, Massachusetts, USA, 1995.

11. Andersson, B., Blomqvist, P., Dederichs, A., “Thermal breakdown of extinguishing agents”, Department of Fire Safety Engineering and Systems Safety, Lund University, ISRN: LUTVDG/TVBB-3137-SE, 2008.

12. Lönnermark, A., Babrauskas, V., "TOXFIRE . Fire characteristics and smoke gas analysis in under-ventilated large-scale combustion experiments. Theoretical background and calculations", Swedish National Testing and Research Institute, Fire Technology, SP Report 1996:49, 1996.

13. Prucker, S., Meier, W., Stricker, W., "A flat flame burner as calibration source for combustion research: Temperatures and species concentrations of premixed H2/air flames", Review of Scientific Instruments 65, 9, 2908-2911, 1994.

14. Andersson, B., Holmstedt, G., "Undersökning av släckeffektivitet och eventuell skadeverkan på människa och utrustning vid användning av släckmedlet NOVEC1230", Department of Fire Safety Engineering, Lund University, Report 7028, 2006 (In Swedish).

15. Su, J. Z., Kim, A. K., Mawhinney, J.R., "Review of total flooding gaseous agents as Halon 1301 substitutes", Journal of Fire Protection Engineering 8, 45-64, 1996.

16. Safety Data Sheet, Kidde Aerospace – Halon 1301. 12 Oct 2007.

17. Isaksson, S., Simonson, M., Holmstedt, G., "Gasformiga alternativ till halon som släckmedel", SP Rapport 1997:10, 1997 (in Swedish).

18. Rivers, P., E,. "Advancement in sustainable fire suppression development C_6F-ketone: A novel new Halon replacement alternative to HFCs and PFCs", Halon Options Technical Working Conference 24-26 April 2001, 341-348, 2001.

19. Babushok, V., Noto, T., Burgess, D. R .F., Hamins, A., Tsang, W., "Influence of CF_3I, CF_3Br and CF_3H on the high-temperature combustion of methane", Combustion and Flame 107, 351-367, 1996.

20. Gardon, R., "An instrument for the direct measurement of intense thermal radiation", The Revue of Scientific Instruments 24, 5, 366-370, 1953.

21. Pitts, W. M., Murthy, A. V., de Ris, J. L., Filtz, J-R., Nygård, K., Smith, D., Wetterlund, I., "Round robin study of total heat flux gauge calibration at fire laboratories", Fire Safety Journal 41, 459-475, 2006.

22. Gunners, N.E., "Methods of measurement and measuring equipment for fire tests", National Swedish Institute for Materials Testing, Fire Engineering Laboratory, 1967:1, 1967.

23. Vikelsøe, J., Johansen, E., "Estimation of dioxin emission from fires in chemicals", Chemosphere 40, 165-175, 2000.

24. NT FIRE 047, “Combustible products: Smoke gas concentrations, Continuous FTIR analysis”, Nordtest, 1993-05, 1993.

25. Hakkarainen, T., Mikkola, E., Laperre, J., Gensous, F., Fardell, P., Le Tallec, Y., Baiocchi, C., Paul, K., Simonson, M., Deleu, C., Metcalf, E., “Smoke gas analysis by Fourier transform infrared spectroscopy – Summary of the SAFIR project results”, Fire and Material 24, 101-112, 2000.

26. Östman, B. “Smoke and soot”, In Babrauskas, V. and Grayson, S. J., (ed.) “Heat release in fires”, New York, Elsevier, chapter 8, 233-250, 1992.

27. Babrauskas, V., 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, 1986.

28. ISO 5660-1:1993, “Fire tests – Reaction to fire – Part 1: Rate of heat release from building products (cone calorimeter method)”, International Organization for Standardization, 1993.

29. Babrauskas, V., “From bunsen burner to heat release rate calorimeter”, In: Babrauskas V, and Grayson S. J., (ed.), “Heat release in fires”, New York, Elsevier, chapter 2, 7–29, 1992.

30. Thornton, W. M., “The relation of oxygen to the heat of combustion of organic compounds”, Philosophical Magazine and Journal of Science 33, 196, 196-203, 1917.

31. 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.

32. Janssens, M., Parker, W. J., “Oxygen consumption calorimetry”, In: Babrauskas V, and Grayson S. J., (ed.), “Heat release in fires”, New York: Elsevier, chapter 3, 31–59, 1992.

33. McCaffrey, B. J., Heskestad, G., “A robust bidirectional low-velocity probe for flame and fire application”, Combustion and Flame 26, 125-127, 1976.

34. Huggett, C., “Estimation of rate of heat release by means of oxygen consumption measurements”, Fire and Materials 4, 2, 61-65, 1980.

35. 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.

36. Neij, H., Thesis "Fluorescence for precombustion diagnostics in spark-ignition engines", ISRN: LUTFD"/TFCP- 41-SE, 1998.

37. Andersson, Ö., Thesis "Development and application of laser techniques for studying fuel dynamics and NO formation in engines", ISRN: LUTFD"/TFCP-61-SE, 2000.

38. Babrauskas, V., Parker, W. J,. Mullholland, G., Twilley, W. H., "The phi meter: A simple, fuel-independent instrument for monitoring combustion equivalence ratio", Revue of Scientific Instruments 65, 7, 2367-2375, 1994.

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

40. Beyler, C. L., "Major species production by diffusion flames in a two-layer compartment fire environment", Fire Safety Journal 10, 1, 47-56, 1986.

41. Sivathanu, Y. R., Faeth, G. M., "Generalized state relationships for scalar properties in non-premixed hydrocarbon/air flames", Combustion and Flame 82, 211-230, 1990.

42. Tewarson, A., "Generation of heat and chemical compounds in fires", In the SFPE Handbook of Fire Protection Engineering, 2nd ed., (Di Nenno, P. J. Ed.) 3:53-124, NFPA, Quincy, Massachusetts, USA, 1995.

43. Tewarson, A., Jiang F. H., Morikawa, T., "Ventilation-controlled combustion of polymers", Combustion and Flame 95, 151-169, 1993.

44. Kawagoe, K., "Fire behaviour in rooms", Report of the Building Research Institute, No 27, September 1958.

45. Babrauskas, V., "Fire endurance in buildings", Report No UCB FRG 76-16, November 1976, Fire Research Group, University of California, Berkeley, USA, 1976.

46. Prahl, J., Emmons, H. W., "Fire induced flows through an opening", Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts, USA, Technical Report No. 12, 1975.

47. Salicone, S., "Measurement uncertainty – An approach via the mathematical theory of evidence", Springer Science and Business Media, 2007.

48. IEC-ISO, "Guide to the expression of uncertainty in measurement", 1992.

49. Taylor, B. N., Kuyatt, C. E., "Guidelines for evaluating and expressing the uncertainty of NIST measurement results", NIST Technical Note 1297, 1994.

50. Pitts, W. M., Braun, E., Peacock, R. D., Mitler, H. E., Johnsson, E. L. Reneke, P. A., Blevins, L. G., "Temperature uncertainties for bare-bead and aspirated thermocouple measurements in fire environments", Combustion Institute Proceedings, Joint Meeting, Washington DC, March 1999, 508-511, 1999.

51. Blevins, L. G., "Modeling of thermocouple behavior in Room Fires", Annual Conference on Fire Research, NISTIR 6242, 1998.

52. Warnatz, J., Maas, U., Dibble, R. W., "Combustion", Springer Verlag, Berlin, 1996.

53. ISO 14934-1, "Fire tests – Calibration and use of heat flux meters – Part 1: General principles", International Organization for Standardization, 2002.

54. ISO 14934-2, "Fire tests – Calibration and use of heat flux meters – Part 2: Primary calibration methods", International Organization for Standardization, 2006.

55. Axelsson, J., Andersson, P., Lönnermark, A., van Hees, P., Wetterlund, I., "Uncertainties in measuring heat and smoke release rates in the room/corner test and the SBI", SP Report 2001:04, Fire Technology, Borås, 2001.

56. Mulholland, G. W., Johnsson, E. L., Fernandez, M. G., Shear, D. A., "Design and testing of a new smoke concentration meter", Fire and Materials 24, 231-243, 2000.

57. Enright, P. A., Fleischmann, C. M., "Uncertainty of heat release rate calculation of the ISO5660-1 cone calorimeter standard test method", Fire Technology 35, 2, 153-169, 1999.

58. Yeager, R. W., "Uncertainty analysis of energy release rate measurement for room fires", Journal of Fire Sciences 4, 276-296, 1986.

59. Sette, B. J. G., Theuns, E., Merci, B., Vandevelde, P., "Temperature effects on the mass flow rate in the SBI and similar heat-release rate test equipment", Fire and Materials 31, 53-66, 2007.

60. Bryant, R. A., Mulholland, G. W., "A guide to characterizing heat release rate measurement uncertainty for full-scale fire tests", Fire and Materials 32, 121-139, 2008.

61. Pitts, W. M., "The global equivalence ratio concept and the formation mechanisms of carbon monoxide in enclosure fires", Progress in Energy and Combustion Science 21, 3, 197-237, 1995.

62. Pitts, W. M., "Application of thermodynamic and detailed chemical kinetic modeling to understanding combustion product generation in enclosure fires", Fire Safety Journal 23, 271-303, 1994.

63. 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, 1997.

64. Tolocka, M. P., Richardson, P. B., Houston Miller, J., "The effect of global equivalence ratio and post flame temperature on the composition of emissions from laminar ethylene/air diffusion flames", Combustion and Flame 118, 521-536, 1999.

65. Drysdale, D., "An introduction to fire dynamics", John Wiley and Sons, ISBN 0-471- 90613-1, 1985.

66. Zeldovich, Y. B., "The oxidation of nitrogen in combustion and explosions", Acta Physicochem, USSR, 21:557, 1946, in [52].

67. Fenimore, C. P., "Formation of nitric oxide in premixed hydrocarbon flames", 13th Symposium (International) on combustion, The Combustion Institute, Pittsburgh, 373-380, 1971.

68. Fenimore, C. P. "Studies of fuel-nitrogen species in rich flame gases", 17th Symposium (International) on combustion, the Combustion Institute, Pittsburgh, 661-670, 1978.

69. Glassman, I., "Combustion Third Edition", Academic Press, San Diego, USA, 1996.

70. Bowman, C. T., "Control of combustion-generated nitrogen oxide emissions: Technology driven by regulation", 24th Symposium (International) on Combustion, the Combustion Institute, Pittsburgh, 859-878, 1992.

71. Wolfrum, J., "Bildung von Stickstoffoxiden bei der Verbrennung", Chemie-Ingenieur-Technic 44:656, 1972, in [52].

72. Malte, P. C., Pratt, D. T., "Measurement of atomic oxygen and nitrogen oxides in jet-stirred combustion", 15th Symposium (International) on Combustion, the Combustion Institute, Pittsburgh, 1061-1070, 1974.

73. Glarborg, P., Miller, J. A., Kee, R. J., "Kinetic modeling and sensitivity analysis of nitrogen oxide formation in well-stirred reactors", Combustion and Flame 65, 177-202, 1986.

74. Dagaut, P., Glarborg, P., Alzueta, M. U., "The oxidation of hydrogen cyanide and related chemistry", Progress in Energy and Combustion Science 34, 1-46, 2008.

75. Smith-Hansen, L., Haahr Jørgensen, K., "Combustion of chemical substances and the impact on the environment of the fire products, micro scale experiments", Risø-R-651, 1992.

76. Fadli, A., Briois, C., Baillet, C., Sawerysyn, J-P., "Experimental study on the thermal oxidation of chlorobenzene at 575-825°C", Chemosphere 38, 12, 2835-2848, 1999.

77. Higgins, B., Thomson, M. J., Lucas, D., Koshland, C. P., Sawyer, R. F., "An experimental and numerical study of the thermal oxidation of chlorobenzene", Chemosphere 42, 5-7, 703-717, 2001.

78. Hirschler, M., "Hydrogen chloride evolution from the heating of poly (vinyl chloride) compounds", Fire and Materials, 29, 367-382, 2005.

79. Galloway, F. M., Hirschler, M. M., "A model for the spontaneous removal of airborne hydrogen chloride by common surfaces", Fire Safety Journal 14, 251-268, 1989.

80. Wang, Z., Jia, F., Galea, E. R., Patel, M. K., Ewer J., "Predicting HCl concentrations in fire enclosures using an HCl decay model coupled to a CFD-based fire field model", Fire and Materials 31, 443-461, 2007.

81. Ewer, J., Galea, E. R., Patel, M. K., Taylor, S., Knight, B., Petridis, M., "Smartfire: an intelligent CFD based fire model", Journal of Fire Protection engineering 10, 1, 13-27, 1999.

82. Ditch, B. D., "Thermal decomposition products testing with 1,1,1,2,2,4,5,5,5 nonafluoro-4-trifluoromethyl pentan-3-one (C_6F-ketone) during fire extinguishing" Master thesis, Worcester Polytechnic Institute, 2002.

83. Hynes, R. G., Mackie, J. C., Masri, A. R., "Inhibition of premixed hydrogen-air flames by 2-H heptafluoropropane", Combustion and Flame 113, 554-565, 1998.

84. Linteris, G. T., "Numerically predicted structure and burning velocity of premixed CO-Ar-O_2-H_2 flames inhibited by CF_3H", Combustion and Flame 107, 72-84, 1996.

85. Shebeko, Y. N., Azatyan, V. V., Bolodian, I. A., Navzenya, V. Y., Kopylov, S. N., Shebeko, D. Y., Zamishevski, E. D., "The influence of fluorinated hydrocarbons on the combustion of gaseous mixtures in a closed vessel", Combustion and Flame 121, 542-547, 2000.

86. Burgess, D. R., Zachariah, M. R., Tsang, W., Westmoreland, P. R., "Thermochemical and chemical kinetic data for fluorinated hydrocarbons", Progress in Energy and Combustion Science 21, 453-529, 1996.

87. Hynes, R. G., Mackie, J. C., Masri, A. R., "Shock-tube study of the pyrolysis of the halon replacement molecule CF_3CHFCF_3", The Journal of Physical Chemistry 103, 54-61, 1999.

88. Hynes, R. G., Mackie, J. C., Masri, A. R., "Sample probe measurements on a hydrogen-ethane-air-2-H-heptafluoropropane flame", Energy & Fuels 13, 485-492, 1999.

89. Vandooren, J., Nelson da Cruz, F., Van Tiggelen, P. J., "The inhibiting effect of CF_3H on the structure of a stoichiometric $H_2/CO/O_2/Ar$ flame", 22nd Symposium (International) on combustion, the Combustion Institute, Pittsburgh, 1587-1595, 1988.

90. Babushok, V., Tsang, W., "Inhibitor rankings for alkane combustion", Combustion and Flame 123, 488-506, 2000.

91. Kim, A. K., Su, J. Z., "Full-scale evaluation of halon replacement agents", Journal of Fire Protection Engineering 10, 1-23, 1999.

92. Holmstedt, G., Andersson, P., Andersson, J., "Investigation of scale effects on Halon and Halon alternatives regarding flame extinguishing, inerting concentration and thermal decomposition products", Proceedings of the 4th International Symposium of the IAFSS, Ottawa, Canada, 853-864, 1994.

93. ISO 19706:2007(E), "Guidelines for assessing the fire threat to people", ISO, ISO 19706:2007(E), 2007.

94. ISO/TS 13571:2002(E), "Life-threatening components of fire – Guidelines for the estimation of time available for escape using fire data", ISO, ISO/TS 13571:2002(E), 2002.

95. Kimmerle, G., "Aspects and methodology for the evaluation of toxicological parameters during fire exposure", Journal of Fire and Flammability – Combustion Toxicology supplement 1, 1974.

96. Arbetsmiljöverket, "Hygieniska gränsvärden och åtgärder mot luftföroreningar", AFS 2005:17, 2005 (in Swedish).

97. NIOSH, “NIOSH Chemical listing and documentation of revised IDLH values (as of 3/1/95)”, 1995.

98. ISO/TR 9122-1:1989, “Toxicity testing of fire effluents – Part 1: General”, ISO, ISO/TR 9122-1:1989, 1989.

99. Jin, T., ”Visibility through fire smoke”, Journal of Fire and Flammability 9, 135-155, 1978.

100. Jin, T., “Visibility and human behaviour in fire smoke”, in the SFPE Handbook of Fire Protection Engineering, 3rd ed., (Di Nenno, P. J. Ed.) 2:42-53, NFPA, Quincy, Massachusetts, USA, 2002.

101. Frantzich, H., Nilsson, D., “Evacuation experiments in a smoke filled tunnel”, Proceedings of the 3rd international symposium on human behaviour in fire, Belfast, UK, 229-238, 2004.

102. Documentation for immediately dangerous to life or health concentrations, National Institute for Occupational Safety and Health (NIOSH), USA, 1994.

103. Hartzell, G. E., Priest, D. N., Switzer, W. G., “Modeling of toxicological effects of fire gases: II Mathematical modeling of intoxication of rats by carbon monoxide and hydrogen cyanide”, Journal of Fire Sciences 3, 115-128, 1985.

104. ISO 13344. “Estimation of the lethal toxic potency of fire effluents”, International Organization for Standardization, 2004.

105. ASTM E1678, “Standard test method for measuring smoke toxicity for use in fire hazard analysis”, ASTM International, 2009.

106. NFPA 269, “Standard test method for developing toxic potency data for use in fire hazard modeling”, National Fire Protection Association, 2007.

107. Levin, B. C., Paabo, M., Gurman, J. L., Harris, S. E., “Effects of exposure to single or multiple combinations of the predominant toxic gases and low oxygen atmospheres produced in fire”, Fundamental and Applied Toxicology 9, 236-250, 1987.

108. Levin, B. C., Paabo, M., Gurman, J. L., Harris, S. E., Braun, E., “Toxicological interactions between carbon monoxide and carbon dioxide”, Toxicology 47, 135-164, 1987.

109. Levin, B. C., “New research avenues in toxicology: 7-gas N-gas model, toxicant suppressants, and genetic toxicology”, Toxicology 115, 89-106, 1996.

110. Schubach, S., "A measure of human sensitivity in acute inhalation toxicity", Journal of Loss Prevention in the Process Industry 10, 5-6, 309-315, 1997.

111. Lees, F. P., "Loss prevention in the process industries", Butterworths, London 1996.

112. Purser, A. A., "Physiological effects of combustion products", Proceedings of the hazards of combustion products: toxicity, opacity, corrosivity and heat release conference, London, UK, 97-122, 2008.

113. Koivisto, R., Nielsen, D., "Fire – a database on chemical warehouse fires", Journal of Loss Prevention in the Process Industry 7, 3, 209-215, 1994.

114. Hietaniemi, J., Mikkola, E., "Minimising fire risks at chemical storage facilities – Basis for the guidelines for safety engineers", Technical Research Centre of Finland, VTT – Research Notes 1811, 1997.

115. Magnusson, B., "Pesticide fire – a human health hazard?: toxicological assessment of pesticide pyrolysis products", Defence Research Establishment, FOA, Umeå, Sweden, Report 273, 1996.

116. Karlsson, L., "Pesticide fire – a human health hazard?: human hazards arising from burning pesticides inert to pyrolysis", Defence Research Establishment, FOA, Umeå, Sweden, Report 274, 1996.

117. Lilliehöök, B., "Pesticide fire – a human health hazard?: pesticides and fire products in smoke", Defence Research Establishment, FOA, Umeå, Sweden, Report 275, 1996.

118. Särdqvist, S., "An Engineering Approach to Fire-Fighting Tactics", Dept. of Fire Safety Engineering, Lund University, ISSN 1102-8246, ISRN LUTVDG/TVBB--1014—SE, 1996.

119. Blomqvist, P., Hertzberg, T., Tuovinen, H., Arrhenius, K., Rosell, L., "Detailed determination of smoke gas contents using a small-scale controlled equivalence ratio tube furnace method", Fire and Materials 31, 495-521, 2007.

120. Hull, T. R., Stec, A. A., Lebek, K., Price, D., "Factors affecting the combustion toxicity of polymeric materials", Polymer Degradation and Stability 92, 2239-2246, 2007.

121. Stec, A. A., Hull, T. R., Lebek, K., Purser, J. A., Purser, D. A., "The effect of temperature and ventilation condition on the toxic product yields from burning polymers", Fire and Materials 32, 49-60, 2008.

122. Thomas, P. H., “Dimensional analysis: a magic art in fire research?”, Fire Safety Journal 34, 111-141, 2000.

123. Quintiere, J. G., “Scaling applications in fire research”, Fire Safety Journal 15, 3-29, 1989.

124. Balthasar, M., Mauss, F., Knobel, A., Kraft, M., “Detailed modeling of soot formation in a partially stirred plug flow reactor”, Combustion and Flame 128, 395-409, 2002.

125. Tuovinen, H., Blomqvist, P., Saric, F., “Modelling of hydrogen cyanide formation in room fires”, Fire Safety Journal 39, 737-755, 2004.