Assessment of fires in chemical warehouses. An overview of the TOXFIRE project

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Assessment of Fires in Chemical Warehouses
An overview of the TOXFIRE project

Editors: Kurt E. Petersen, Frank Markert

Risø National Laboratory, Roskilde, Denmark
May 1999

Abstract

The report summarises the scientific outcome of the CEC Environment project "TOXFIRE. Guidelines for Management of Fires in Chemical Warehouses". The project was performed in the period 1994 - 1996 in a multi-national co-operation between partners from United Kingdom, Sweden, Finland and Denmark. The project included micro, small, medium, and two types of large scale combustion experiments. The experiments focused on the characterisation of the combustion products and scaling effects are described. Additional, a few experiments on the effects of packaging and water on the fire products have been performed. Also included were items as fire modelling, risk assessment to human health and the environment. Finally, the basis of guidelines for safety engineers and fire brigades were established.

The report describes the work done by each partner and the main results achieved. The references of all reports from the TOXFIRE project are listed.

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1 Introduction

In many countries there are a large number of chemical plants and storage facilities that handle and store substantial amounts of hazardous substances, e.g. pesticides. Chemical fires seem to be one of the most important hazards from these activities. Today only limited documentation is available concerning the assessment of the potential consequences from fires at chemical plants and storage facilities. The project *Guidelines for Management of Fires in Chemical Warehouses* (TOXFIRE) was initiated in order to remedy some of these problems. The project is financially supported by the CEC ENVIRONMENT programme (contract no. EV5V-CT93-0275). The project was carried out by an international consortium during a three years period (1993-1996) including the following partners (abbreviation of the respective names in parentheses):

Risø National Laboratory, Denmark, co-ordinator (Risø)

Danish National Environmental Research Institute (NERI)

South Bank University, United Kingdom (SBU)

Technical Research Centre of Finland, (VTT)

Lund University, Sweden (LU)

Swedish National Testing and Research Institute (SP)

Swedish Defence Research Establishment (FOA)

Based on a number of characteristics the substances can be classified comprising ignitability, heat release, burning rate, smoke evolution, combustion products and the influence of the packaging materials on the combustion products. The source characteristics can be described by parameters obtained by carrying out combustion experiments at various scale and by studying the effects of scaling. In addition, the fire scenarios can be characterised by the degree of ventilation, the packaging materials, the stacking of the materials and the response of the building. Also the suppression is an important parameter, i.e. active and passive suppression and the fire brigade tactics. Obviously, the consequences to humans as well as to the environment are essential. The investigation in the present project are leading to the development of the basis for two sets of guideline documents in relation to fires in chemical warehouses: guidelines for the safety engineers and guidelines for the fire brigades. In parallel also a quick decision system to be used by the fire chief in case of chemical fire is developed. This report contains a summary of the results obtained in the project and a full list of references to reports, articles and conference papers where all the details from the experimental and modelling work are presented.

2 List of Participants

In the following list all the participants involved with the TOXFIRE project are named in alphabetical order. The contact persons for each contribution are given in the respective chapters, where also the addresses can be found.

Andersson	Berit	Department of Fire Safety Engineering; LU
Blomqvist	Per	Chemical Analysis, SP
Fredholm	Lars	Swedish War College and FOA ; Sweden
Jørgensen	Klaus Haahr	Combustion Department, Risø
Hardy	Alain	Chemical Engineering Research Centre, SBU
Hietaniemi	Jukka	Building Technology; Fire Technology, VTT
Holmstedt	Göran	Department of Fire Safety Engineering; LU
Isaksson	Ingrid	Chemical Analysis, SP
Johansson	Per-Erik	Division of NBC Defence, FOA
Kakko	Rhea	Manufacturing Technology; Safety Engineering, VTT
Kallonen	Raija	Building Technology; Fire Technology, VTT
Karlsson	Lena	Division of NBC Defence, FOA
Könberg	Mats	Division of NBC Defence, FOA
Lautkaski	Risto	Energy Systems, VTT
Lilliehöök	Bo	Division of NBC Defence, FOA
Lönnermark	Anders	Fire Technology, SP
Magnusson	Beatrice	Division of NBC Defence, FOA
Månsson	Margret	Chemical Analysis, SP
Markert	Frank	Systems Analysis Department, Risø
McIntosh	Roderick	Chemical Engineering Research Centre, SBU
Mikkola	Esko	Building Technology; Fire Technology, VTT
Nolan	Philip	Chemical Engineering Research Centre, SBU
Persson	Henry	Fire Technology, SP
Petersen	Kurt E.	Systems Analysis Department, Risø
Powell	Simon	Chemical Engineering Research Centre, SBU
Rasmussen	Birgitte	Systems Analysis Department, Risø
Rosell	Lars	Chemical Analysis, SP
Särdqvist	Stefan	Department of Fire Safety Engineering; LU
Smith-Hansen	Lene	Systems Analysis Department, Risø
Svensson	Stefan	Swedish Rescue Service Agency
Vikelsøe	Jørgen	Department of Environmental Chemistry, NERI
Winter	Göran	Department of Fire Safety Engineering; LU
Winter	Stellan	Division of NBC Defence, FOA

On Sunday 12 February 1995, Lene Smith-Hansen from Risø National Laboratory died after a few days of illness. Lene was co-ordinator of the TOXFIRE project and did her work on chemical warehouse fires with talent and enthusiasm, giving her a prominent position within this research area in Europe. She will be missed by a number of colleagues in Europe and in particular by the staff at Risø.

3 Structure of the project

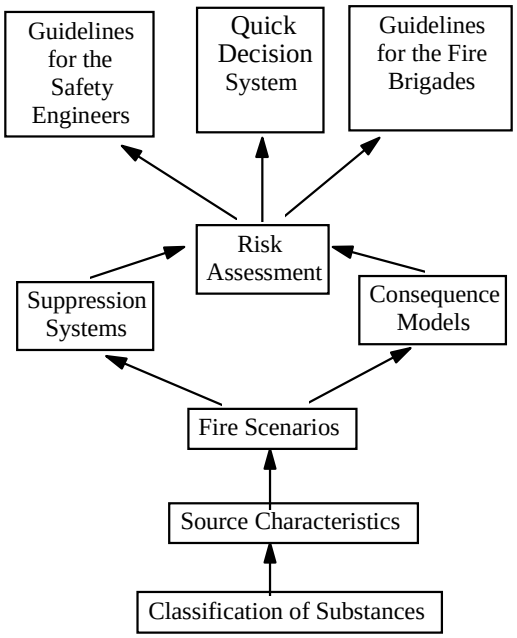
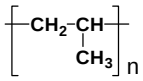
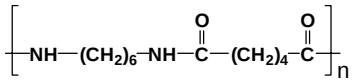
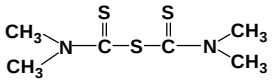
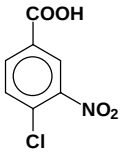
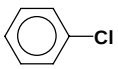


Figure 1 Items of the TOXFIRE project

In chapter 1 the objectives of the TOXFIRE project are described. The project (see Figure 1) had an experimental part in which e.g. the source characteristics, the influence of packaging materials, water sprinkling, the scaling and dioxin formation are investigated. Substances were chosen to be tested in all scales and are listed in Table 1. The second part of the project involved modelling, e.g. the development of a fire spread model, surveys on models used to be able to perform an ecotoxicological risk assessment and the assessment on human health. The third part of the project was to establish the basis for guidelines for safety engineers and the fire brigades. Also a software tool "Quick decision system" to be used during fire emergencies was developed and tested.

The experimental part was subdivided into the items "classification of substances" and "source characteristics" shown in Figure 1 and are more detailed described in chapter 4. The second part on modelling includes the items "fire scenarios", "suppression systems", "risk assessment" and "consequence models". The main results are described in chapter 5. The third part on the basis for guidelines is described in chapter 6 and includes the three items "guidelines for the safety engineers and the fire brigades" and the "quick decision system".

Table 1: The five substances used in the scaling experiments

Polypropene **PP – $[C_3H_6]_n$**	
Nylon 66 **NY – $[C_{12}H_{22}N_2O_2]_n$**	
Tetrametylthiuram monosulfide **TMTM – $C_6H_{12}N_2S_3$**	
4-Chloro-3-nitro-benzoic acid **CNBA – $C_7H_4NO_4Cl$**	
Chlorobenzene **CB – C_6H_5Cl**	

4 Experimental part

4.1 Screening of Substances and Micro-scale Experiments

Risø [1]/Frank Markert

Screening of Substances

A screening of substances was performed applying “flash pyrolysis” experiments. The equipment used was a pyrola flash pyrolysis unit linked to a Varian II GC/MS system. The substances (about 100 µg) were placed on a platinum foil operated at 150°C and were purged with helium. Then the probe was flash pyrolysed at 900°C with a heating rate of 10^4 - 10^5 °C/s for a duration of about 2 s. The decomposition products were analysed by the linked GC/MS system.

The obtained information from these experiments were e.g. an upper limit for the survival fractions. Such information was used to find relevant substances for the combustion experiments.

In the project a large number of substances have been pyrolysed and the following major patterns have been observed:

- Pyrolysis gives a greater variety of organic products compared with the DIN 53436 furnace.
- Organic products from the DIN 53436 furnace are a subset of those from the pyrolysis

[1] Risø National Laboratory, Systems Analysis Department, P.O. Box 49, DK-4000 Roskilde, Denmark

- Aromatic products from all compounds, like benzene, toluene, phenanthrene/anthracene are generated.
- A majority of the nitrogen-containing pesticides produced benzonitrile, which therefore might be a key component.

Micro-scale experiments

The DIN 53436 furnace was used for the combustion experiments. The method is intended to simulate steady-state conditions. The furnace has been slightly modified in order to ensure a constant production of combustion gases. A similar modification has also been described in the literature.

The DIN 53436 furnace (see Figure 2) consists of a quartz combustion tube (length 1 m, diameter 4 cm) and a movable (1 cm/minute) annular electric oven enclosing a section of the tube. The sample (1-3g) is placed in 24 small vessels posed in a 40-cm quartz boat. Air flows through the quartz tube during the experiment and transports the combustion products into the FTIR equipment. A Bomem MB100 FTIR instrument was used for on-line gas analyses in the experiments. The instrument was equipped with a multiple-pass gas cell (0.7 l volume) operated at 180 °C and a pathlength of 6.4 m.

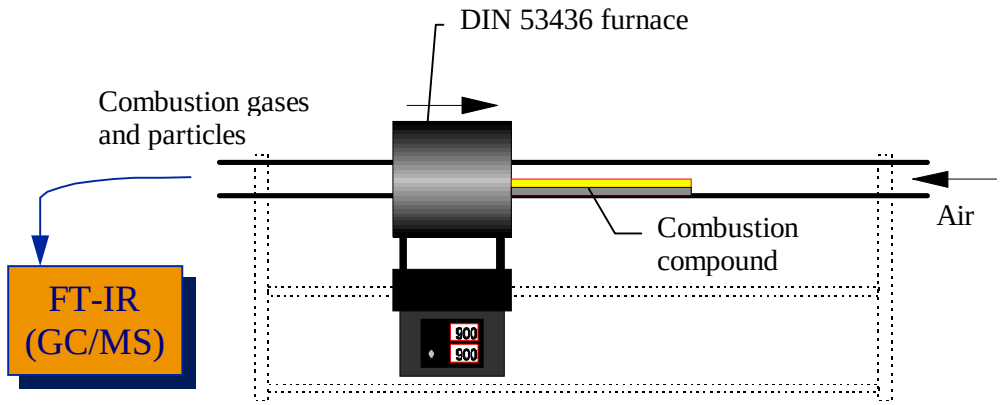


Figure 2: Setup of the DIN 53436 furnace

Experiments have been performed with the substances chosen from the screening, including the five substances chosen to be burned in all scales. In order to simulate different fire conditions due to the ISO classification, furnace temperatures of 500 and 900 °C were applied. At these temperatures experiments were conducted under three different ventilation conditions each, with 100 l/h air, 50 l/h air and 50l/h air mixed with 50 l/h nitrogen. The conditions are chosen to simulate non-flaming decomposition and fully developed fires at different degrees of ventilation.

On-line FTIR measurements were used to quantify combustion gasses like CO_2 , CO, $COCl_2$, HCN, N_2O , NO, NO_2 , SO_2 and HCl. Off-line GC/MS measurements were mainly used to analyse for organic combustion products. The yields are reported as gram combustion product per gram fuel to be comparable with the other experimental results. By this, valuable information on combustion products for e.g. pesticides have been compiled under different fire conditions. The tubular furnace could be applied to all the substances and under a wide range of conditions. The results for each

substance burned are compared to the other scale results. The scaling results are more detailed described in chapters 4.5 and 4.6.

4.2 Small Scale Cone Calorimeter Experiments

VTT [2]/ Jukka Hietaniemi, Raija Kallonen

The cone calorimeter technique was employed to investigate the burning characteristics and composition of fire effluents of selected chemicals, including pesticides, compounds used in chemical industry, a liquid solvent and polymers. A controlled-atmosphere apparatus was utilised, allowing to vary the ventilation conditions in the test chamber.

The quantities measured to determine the burning properties were time to ignition, rate of heat release, mass of the sample and its rate of change and the smoke production. Also several quantities characterising *e.g.* the combustion efficiency were derived. The composition of the fire effluents was determined by FTIR spectroscopy and GC/MS analysis. With some substances the influence of extinction with a water spray was studied.

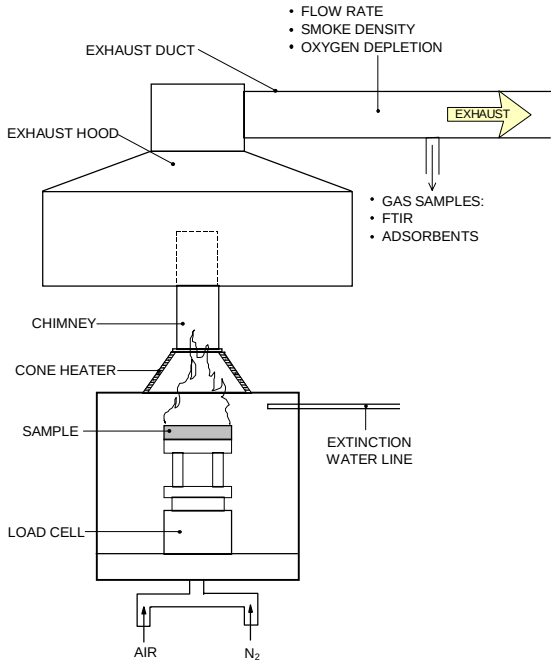


Figure 3 The cone calorimeter setup

The burning characteristics and the combustion efficiency of the substances were primarily affected by the chlorine contents of the substance. The influence of the ventilation conditions was smaller.

[2] VTT Building Technology/ Fire Technology, P.O. Box 1803,FIN- 02044 VTT, Finland

Vitiation of the combustion atmosphere seemed to affect the burning characteristics only at rather low O_2 percentages. Lowering the O_2 percentage from 21 % to 15 % diminished the burning intensity only slightly. A further decrease to 12.5 % caused decrease in the heat release rates; for some compounds burning was quenched completely. The smoke production remained virtually unaltered by the O_2 percent for all compounds.

Yields of most of the combustion gases (CO_2, CO, HCN and HCl) were found to be correlated to the combustion efficiency. Exceptions to this correlation scheme were constituted by nitrogen oxides.

The fractions of the parent substances escaping the fire without decomposing (survival fraction) and abundances of some decomposition products were determined by GC/MS analysis. The survival fractions detected varied considerably: some compounds decomposed completely while for some substances the survival fraction was high, up to 20 % of the burned mass.

According to the results, the influence of water extinction on the fire-effluent toxicity may be divergent. On one hand, it may lead to elevated toxicity through increased production of CO, HCN and some nitrogen oxides, and on the other hand, water extinction may have a cleansing influence on the high-molecular constituents of the exhaust gases.

4.3 Medium-scale Experiments

Lund [3] / Berit Andersson

Experiments have been performed in a combustion chamber in medium scale. The internal dimensions of the combustion chamber were 0.75 m (width), 1.10 m (depth) and 0.80 m (height) which is approximately 1/3 of the standard ISO room corner test. The volume of the chamber was 0.66 m^3. Tests were performed under a number of different conditions. The variables were: ventilation, external radiation (0, 4.2, 22.4 kW/m^2), pool diameter (0.1 to 0.4 m) and substance burned.

During the tests a number of continuous measurements were made. Continuously measured gases were: O_2 (paramagnetic technique), CO_2 and CO (IR technique), NO_x (chemiluminiscens technique) and unburned hydrocarbons (flame ionisation technique). Other parameters measured continuously were: smoke, massloss and phi-value (ventilation parameter). The on-line measurements were made in the exhaust duct and in the opening to the room.

[3] Lund University, Institute of Technology, Department of Fire Safety Engineering, P.O. Box 118, S-221 00 Lund, Sweden

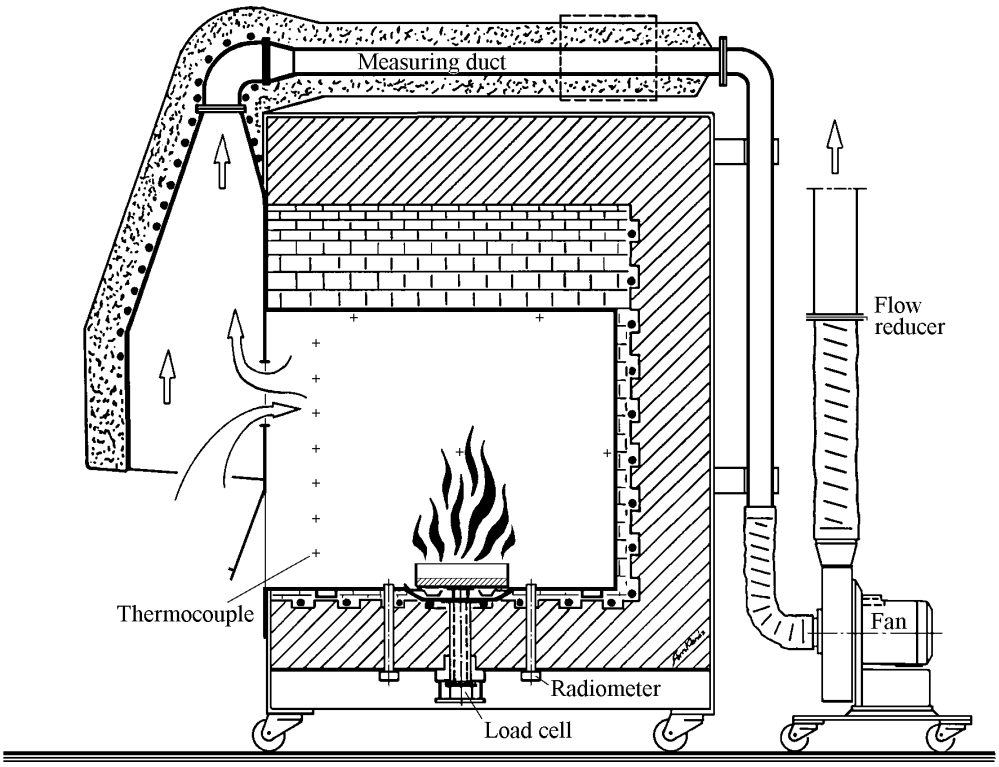


Figure 4 The 1/3 room-scale setup

Inside the combustion chamber measurements were made of temperatures and of radiation to the floor. The mass of the tested substance was also measured throughout the experiment in order to determine the massloss. This is an important parameter since other parameters are normalised against the massloss. Intermittently gas samples and soot samples were collected iso-kinetically from the exhaust duct. The gas samples were analysed with gas chromatography-mass spectroscopy in order to determine the fraction of the burned substance that survived the test and also to find the main products which were formed during the combustion. Analysis of the gas samples were also made with ion-chromatography to determine the amounts of Cl, HCN, P and SO_x in the exhaust gases. The amount of smoke produced during the experiments was measured optically in the exhaust duct. Soot was also collected intermittently on a filter during a period of the test when the burning was relatively constant. From these measurements the mass of soot per mass burned substance can be determined.

Tests have been performed with heptane, chlorobenzene, tetramethylthiuram monosulfide (TMTM), 4-chloro-3-nitrobenzoic acid (CNBA), dimethoate, nylon and polypropylene. The chosen substances are all organic compounds. Dimethoate is a pesticide, TMTM, CNBA and chlorobenzene are substances of pesticide type with heteroatoms like Cl, N, P and S, polypropylene is a polymer used in packaging, nylon is used as a reference substance throughout the project and finally heptane is a fuel with well known performance in fire.

The results are presented as yields (mass of species formed per g substance burned) for CO, CO_2, NO_x, THC and soot. The recovery of for example C and Cl is presented

as well as the combustion efficiency and the temperatures inside the combustion chamber in medium scale.

4.4 Indoor Large-scale Underventilated Fire Tests

SP [4] / Margret Månsson, Henry Persson

The large-scale experiments at SP were conducted over a wide range of ventilation conditions. Most of the combustions were carried out in the ISO 9705 *Full-scale Room*, $3.6 \times 2.4 \times 2.4$ m^3. The degree of ventilation was defined as the equivalence ratio, ϕ, i.e. the ratio of the *'actual fuel to oxygen*' and the *'stoichiometric fuel to oxygen*' ratios.

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

$\phi = 1$ stoichiometric combustion

$\phi < 1$ well-ventilated combustion

$\phi > 1$ under-ventilated combustion

A ϕ -meter was built and used to obtain a direct measure of ϕ. The ventilation conditions were controlled by varying the heights of the door opening, 0.89 m, 0.68 m, 0.56 m and 0.45 m, respectively, and by the sample pan area, from 0.5 m^2 to 1.4 m^2. A load cell, connected to the pans via a pole passing through an opening in the floor, was used to measure the mass loss rate. A thermocouple tree with 15 thermocouples was used to measure the vertical temperature distribution in order to define the density gradient in the room to be used e.g. in calculations of the flow of smoke gases out of the room.

Probes for the gas analysis and ϕ-meter samples were placed diagonally from the top left corner to the centre of the other side of the opening and varied in length depending on the size of the opening. They were stainless steel tubes with a 6 mm inner diameter and had 3 mm diameter holes at distances of 0.10 m, the number of holes depending on the length of the probe. An FTIR spectrometer with a heated 0.9 L gas cell was used for on-line measurements of low molar mass compounds in the smoke exiting through the door opening. In addition, a chemiluminescence instrument was used for on-line measurements of nitrogen oxides, NO_x, and a flame ionisation detector for the total amounts of unburned hydrocarbons, THC. Smoke gases were also drawn through two lines of adsorbents to allow measurements of an extended range of organic components in the smoke. Soot was sampled for defined periods to allow subsequent analysis of its composition.

[4] Swedish National Testing and Research Institute, Chemical Analysis/Fire Technology, P.O. Box 857, S- 50115 Borås, Sweden.

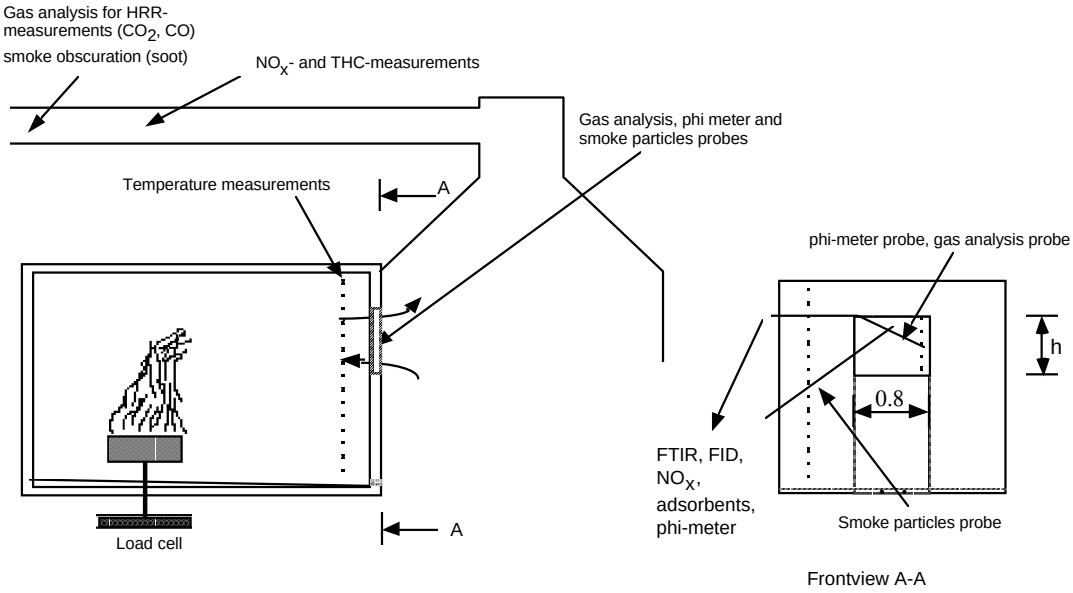


Figure 5 The large -scale experimental setup in the ISO 9705 room, indicating the sampling probe configurations in the door opening and in the exhaust duct.

The combustion gases from the room were collected by a hood leading to an exhaust duct, 0.4 m in diameter, where gas temperature and flow rate were measured, and gas was sampled to the gas analysis equipment for determinations of the concentrations of CO_2, CO, NO_x and THC. A lamp-photocell system measured the light obscuration used to determine the soot production. Together with the duct flow rate, the concentrations of CO_2, CO, THC and soot were used to calculate the HRR values. The mean flow in the duct was at the beginning of each test about 3.2 m^3/s (25.6 m/s).

Five materials were studied: polypropene, Nylon 66, tetramethylthiuram monosulfide, 4-chloro-3-nitro-benzoic acid and chlorobenzene, the last being a volatile liquid, the others being low vapour pressure solids.

To allow a real storage configuration, an even larger test enclosure, $8.9\times6.0\times4.8$ m^3, was built in SP's fire hall, with an opening (0.8×0.89 m^2) on one of the long sides with its upper part 1.5 m from the enclosure ceiling. The substances were packed in small paper bags which were in turn put into cardboard boxes ($0.4\times0.6\times0.5$ m^3). Eight boxes were placed in a two-tier configuration with four boxes on each level. The total amount of substance was 160 kg in each such configuration test. Chlorobenzene had been put into polyethene bottles that were placed in cardboard boxes but could not be safely controlled in such a storage configuration indoor test. Instead, the chlorobenzene test had to be conducted as a pool fire in that case as well.

4.5 Sampling and Analysis of Dioxins

NERI[5] / Jørgen Vikelsøe

In the present study formation of dioxin (PCDD/F) during combustion of a number of chemical substances was measured. The substances, most of which were commonly used chlorine containing pesticides, were selected on the basis of chlorine content and the amounts sold in Denmark annually. Some others were included for reference and for tests in medium and large scale.

The dioxin generation was measured during combustion of 2.5 g of substance in a DIN 53 436 furnace at 500 ºC and 900 ºC. To study scale-up factors, cone calorimeter tests burning 20 g of substance (medium scale), and ISO 9705 room tests burning about 50 kg of substance (large scale) were carried out. 4-chloro-3-nitrobenzoic acid (CNBA) and chlorobenzene (CB) were studied in medium and large scale. In the DIN furnace experiments the total fluegas output was collected in an all-glass sampling train consisting of collector funnel, 2 cold traps and XAD-2 filter. In the cone calorimeter and ISO-room experiments a side stream of the fluegas was sampled iso-kinetically, using nozzle and condenser in place of funnel and first cold trap. After extraction and clean-up, the samples were analysed for PCDD/F using high-resolution GC/MS.

The DIN furnace results summarised in Table 2 (I-TEQ = International Toxic Equivalents) show that some substances emit very large amounts of PCDD/F.

Table 2 Results of DIN Furnace experiments in yields of ng I-TEQ / g substance

Substance	Yield 500 °C	Yield 900 °C	Substance	Yield 500 °C	Yield 900 °C
Atrazin	1.0	0.9	Dimethachlor	6.7	24
Captan	0.6	0.1	Dimethoat	1.7	2.1
Chlormequat-Cl	0.1	0.1	Diuron	5.2	0.5
Chlorobenzene	1.6	4.2	Lindane	0.2	1.3
Chlorothalonil	19	18	MCPA	4.9	0.1
CNBA	7.9	0.6	Pentachlorophenol	740	162
Dichlobenil	nd	nd	PVC	0.1	nd
Dichlorprop	57	1.4	TMTM	0.4	0.7

Pentachlorophenol top the list, followed by Dichlorprop, Chlorothalonil and Dimethachlor. In contrast, Dichlobenil and PVC emit very low amounts. Some heat-stable substances emit the higher amount at the higher temperature, and *vice versa*, but many emit about the same amount at both temperatures. The ratio between the 17 measured 2,3,7,8-substituted PCDD/F congeners (the congener profile, not shown) differed significantly for different types of substances.

The results of the scaling experiments for CNBA and CB are summarised in Table 3. The temperatures for the cone calorimeter are computed from flue gas temperatures.

[5] National Environmental Research Institute, Department of Environmental Chemistry
P.O. Box 358, DK-4000 Roskilde, Denmark

Table 3 Results of scaling experiments in yields of ng I-TEQ / g substance

Exp. type	CNBA weight	T °C	Yield	CB weight	T °C	Yield
DIN furnace	2.5 g	500	7.9	2.5 g	500	1.6
	2.5 g	900	0.6	2.5 g	900	4.2
Cone Cal.	20 g	586	249	20 g	616	21
	20 g	274	94	20 g	279	40
	20 g	910	225	20 g	886	18
	20 g	392	166	20 g	437	37
	20 g	408 *	96	20 g	437 *	743
ISO Room	74.5 kg	204 *	46	45 kg	476 *	4.6
	60 kg	594	9.4	51 kg	872	7.8
	40 kg	353	22	50.5 kg	561	3.7

** extinction with water*

The results for the ISO-room experiments are on the same level as the DIN furnace, and show the same influence of temperature. Surprisingly, the intermediate scale cone calorimeter results are somewhat higher, and the influence of the temperature the opposite of the other experiments.

The study demonstrates that a number of chemicals generate substantial amounts of PCDD/F during combustion, and that large differences between different chemicals exist. It further indicates that dioxin emission during the burning of chemicals may be estimated by means of small scale laboratory tests.

4.6 Scaling Effects

Lund [6]/ Göran Holmstedt

For normal building fires, occurring in, say, a hotel or office room, it is possible to study fire development in the real scale. A technique for doing this has already been standardised as the ISO 9705 fire test room. Such a test room measures 2.4 m by 3.6 m in plan and is available in numerous European fire laboratories. A chemical warehouse fire, however, may be occurring in a building which is vastly larger than such a test room. Such fires are economically impossible to study in the real scale. To develop the proper fire fighting information, it is then necessary to consider fire scaling. That is, a methodology must be established how combustion properties may be developed on the basis of smaller-scale tests, then translated to the real-scale application.

The scales examined in the TOXFIRE program comprise:

Micro-scale. DIN 53 436 tube furnace, by Risø, Denmark.

Bench-scale. ISO 5660 Cone Calorimeter, by VTT, Finland.

1/3-scale room, by Lund University, Sweden.

Room-scale. ISO 9705 room, by SP, Sweden.

[6] Lund University, Institute of Technology, Department of Fire Safety Engineering, P.O. Box 118, S-221 00 Lund, Sweden

The chemicals studied was polypropylene, $(C_3H_6)_n$, nylon 6,6, $(C_{12}H_{22}N_2O_2)_n$ tetramethylthiuram monosulphide (TMTM), $C_6H_{12}N_2S_3$,, 4-chloro-3-nitro-benzoic acid (CNBA), $C_7H_4ClNO_4$ and chlorobenzene, C_6H_5Cl.

For scaling purposes, the primary variable to be examined is the *yield* of various combustion products. For any product, the yield is defined as:

$$f_x = \frac{g\ produced\ of\ product\ x}{g\ fuel\ mass\ lost}$$

Another special yield quantity is the amount of heat produced per mass of fuel lost. This is defined as the *effective heat of combustion.* It represents the actual heat/mass ratio during the particular fire, as contrasted to the heat of (complete) combustion.

Based on these fundamental definitions, the scaling hypothesis tested was: *Is the yield of any substance dependent only on the value of the fuel/air ratio, ϕ, and independent of the scale*. It is known, of course, that many other variables can affect fire behaviour, apart from the fuel/air ratio. These can range from relative humidity and wind velocity to aspects of turbulence, edge conditions and a plethora of other real-world considerations. Fortunately, fully-precise modelling of the fire is not required for fire fighting and consequence modelling purposes. It will be enough to determine whether or not there are significant effects from the fire scale or from other variables.

In the project the hypothesis that the yield of any substance is dependent only on the value of the global fuel/air ratio and independent of scale was found not valid for most of the substances studied.

The following major patterns have been observed:

- Adding heteroatoms (N, S and Cl) to a hydrocarbon can change the yields considerably from ”normal hydrocarbon behaviour”.
- Soot and CO formation from chlorobenzene does not depend on the global fuel/air ratio. Other parameters such as combustion efficiency and upper layer temperature seem to be more important.
- In TMTM fires only a minor fraction of soot is formed.
- The conversion fraction of the Cl in the fuel to HCl is usually high and independent of the global fuel/air ratio.
- Survival fractions vary considerably, some compounds decompose completely while for some substances the survival fraction is high, up to 5-20% of the burned mass.
- A lot of decomposition products including aromatic compounds are formed.
- Dioxin emission is of the same level in different scales.

5 Modelling part

5.1 Effects of Storage Configurations and Fire Spread Models

South Bank [7]/ Philip Nolan, Roderick McIntosh

Evaluation of the effects of fire in a warehouse environment is important in the design of the storage configuration. Data from full-scale fires are relatively sparse, and are expensive to obtain under large or full scale conditions. A number of tests would be needed to fully evaluate various fire situations.

Accordingly, a mathematical model named *CRAFT (Chemical Reactions And Fire (Toxfire))* has been devised allowing evaluation of various scenarios. The nodal model is based on well known heat transfer principles, using finite difference methods to evaluate changing temperatures of each node with time. The associated computer code, written in "C," has been developed to allow versatility in the defined scenarios.

The model assumes an external fire source, which provides incident radiation onto the surface of a stack of drums containing solid materials. The geometry of the stack is variable to allow various permutations to be examined. Heat is transferred through the drums and stack via conduction, convection and radiation, heating up the stored solids. A second stack may be placed at a specified distance from the first, to evaluate separation requirements. Pressure generation due to heating of the gas phase within the drums or evolution of gases from reacting solids will occur. Pressure relief and its effect on temperature and pressure in the drums is incorporated in the model. Reaction of the stored material, such as decomposition, and its effect on heat transfer is included and assumes Arrhenius kinetics to evaluate the heat of reaction. Arrhenius kinetics are also used to estimate changes in concentration of the stored material and the gas generated from the reaction.

The immediate outputs from the model can give, at any instant of time, a temperature profile through the stack and the gas evolution rate in each node. These can be used to predict the pressure in the drum, and the concentration of each node. Since all data are at instants in time, the rates of change of all the parameters can be estimated by comparison at consecutive time steps.

In order to show the general effects of the fire, the model has been run under conditions relevant to sodium chlorate storage in the UK. This has shown that initially, the gas phase heats up quicker than the stored solid, and because of the very low bursting pressure of the vessels, pressure relief occurs before any gas is generated within the solid.

The model has also been run to evaluate various specific effects :

- varying the separation distance between two stacks, where the first stack is maintained at the flame temperature. This can be used to evaluate the required separation distance between the stacks to sufficiently delay fire spread.
- varying the insulation effect offered by the construction material of the drum. Insulating the drum can offer protection to the stored material, and the required thickness of insulation can be estimated.

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- presence of contaminants in the solid. The solid can be contaminated by the construction material of the drum or by any drum linings. The contamination can affect the nature of the reaction.
- full engulfment of the stack by the flame. The effect of insulation on the drum and insulating barriers can be evaluated when the stack itself is on fire.

The results demonstrate the ability of the model to predict the behaviour of the stored solid during the fire. The model has the potential for use in the investigation of current warehouse practice and to evaluate the potential damage caused by a fire.

5.2 Consequence Models for Health Hazards

FOA [8]/ Mats Könberg

This part is concerned with the quantification of the human health hazards arising from fires occurring in stores of a selected group of pesticides. Consideration is given to toxic effects in humans after exposure to the pesticides surviving the pyrolysis conditions from the screening and some of their pyrolysis products.

When studying the human health hazards it is important to notice the difference between dose and concentration. When a substance is administered as a well-defined quantity, e.g. oral or intravenous, the dose is expressed as amount substance per kilo body weight, usually mg/kg. In a warehouse fire, however, the toxic substances appear as gases or aerosols. The dosage is then given by the concentration in the air and the exposure time for each individual.

A value frequently used to describe the acute toxicity of a substance is the dose that results in a 50 % lethality, LD_{50} (Lethal Dose 50 %). If the substance is inhaled the corresponding value is LC_{50} (Lethal Concentration 50 %), which implies an assumption of the time of exposure. In combustion toxicology this time is 30 minutes. The LC values for the chosen pesticides and pyrolysis products were collected from the literature. If possible human LC values were used, but in most cases such data are missing and then the LC values have to be transformed from animal values.

In order to classify the chemicals according to their possible health hazards a method is proposed taking both the toxicity and available amount into account. These calculated toxicity values can be used for screening purposes, as an indication of the toxicity level of the fire smoke or to make a rough comparison of the toxic fire hazards between different pesticides.

In the case of a warehouse fire the formation of toxic products is a complex phenomenon. Depending on the variation of a number of factors, e.g. the oxygen supply and the temperature, the composition of the smoke can not be predicted. The major part of the pesticide will be combusted to simple smoke gases. But one uncertainty factor is that the surviving fraction of the pesticides are unknown. In some cases, also the formed products can be even more toxic than the parental substances and synergistic and additive effects may occur.

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In a consequence model the knowledge of the dispersion of the smoke plume in the air is required. The highest concentrations of toxic fire products will, in most cases, occur close to the fire where most people might have access to some kind of protective equipment. Further away (some hundred meters) unprotected people will be affected. The dispersion calculations show concentrations high enough for causing lethal injuries, in some scenarios. The emission rates in those cases were based on pyrolysis data, however, which may not be representative for a large fire scenario where the chemicals instead will undergo combustion. Dispersion calculations are also used to illustrate the difference in toxicity between the pesticides and the formed pyrolysis products.

A consequence model like this is still subject to assumptions, approximations and large uncertainties. The resulting composition of the smoke is strongly dependent on the fire scenario as the results of the project show. Nevertheless, it has been illustrated that the developed method of estimating the health hazards can be applied in various cases.

5.3 Consequence Models for Ecotoxicological Effects

South Bank [9]/ Philip Nolan, Alain Hardy

The detailed reports of a number of large scale, industrial fires have been reviewed. The particular fires were selected for this study because their products of combustion and survival fractions of the stored materials were of interest in terms of the pollution levels generated and their consequences. In order to address the consequences to the environment, following a major fire, it is necessary to consider the use of a number of sub-models, each dealing with a particular phase of the release. The output of each sub-model feeding into the next sub-model in the fire product release sequence. The sub-models will include:

1. A source term model. This concerns the size of the initial release site for the escape of the fire products, i.e. hole of variable size in roof or vertical wall, or release from open ground, e.g. release following collapse of building walls. In particular, it is necessary to know the mass flow rate of smoke, it's temperature, velocity and the chemical finger-print of the fire products and survival products leaving the release site.
2. A plume rise model: The fire product plume will be thermally buoyant and will rise prior to the dispersion phase.
3. A dispersion model.
4. A deposition model.
5. Possibly a food chain model. Fire products and survival fractions can be deposited on waterways and/or agricultural land. Hence the consequences of the fire may involve consideration of the food chain.

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A number of commercial packages are available to cover phases 3) & 4). Some of these now take the form of geographic information systems, in which the dispersion and deposition can be placed against a map of the location affected.

The selected fires were categorised in terms of their source materials. These were plastics, pesticides and other industrial chemicals. The deposition and subsequent interaction of some of the fire products and survival fractions with plant life, mainly agricultural crops, have been examined. This investigation led to a study of the literature on the damage exhibited by plants involved in controlled pollution experiments, including visible, histopathological microstructure (organelle) and yield-reducing (biomass-reducing) effects.

The main pollutants from the three categories of fires were heavy metals, e.g. cadmium released in a large warehouse storing PVC, chlorinated hydrocarbons, e.g. released in fire involving pesticides, PCB's, polycyclic aromatics and dioxins. The fall-out distance of specific pollutants can be predicted, for given weather conditions. For instance, heavy metal fall-out occurs usually within the immediate vicinity of the warehouse, i.e. if the warehouse is in a factory, the fall-out remains within the factory boundary.

Methods of monitoring the spread of fire product pollutants, both temporally and spatially, have been reviewed, together with a detailed analysis of pollutant behaviour and its variations caused by environmental, i.e. topographical features, and atmospheric conditions.

6 Basis for Guidelines and Quick Decision System

6.1 Guidelines for the Safety Engineers

VTT [10]/ Jukka Hietaniemi, Esko Mikkola

The report addresses fire safety engineering problems of chemical storage facilities. The methodology of the guidelines is based on the ISO/TC 92/SC4 *Fire Safety Engineering* -documents. The basic elements of fire safety design of a chemical warehouse are described: construction design, model fires and fire simulation, storage and packaging, preventive and protective systems, building location and safety distances.

Concerning the design of the warehouse construction, the following items are discussed: compartmentation and structures, escape routes, smoke ventilation and retention of spills and fire fighting water.

Design fires and fire development are discussed with an emphasis on the fire simulation models. Fire behaviour properties of some chemicals are quoted as an example. Analytical tools as well as ones requiring computer calculations are treated.

The influence of the storage layout and packaging on the fire spread and the consequences of fire are discussed. Concerning the warehouse layout the items presented include the effects of the size of the stacks and the separation gap between the stacks. The influence on the fire spread of the physical properties of the packaging and the nature of the materials being stored are dealt with, as well the mechanisms in which packaging can contribute to the fire.

The discussion on the preventive and protective systems includes treatise on alarms and fire detection, sprinklers and other automated means of extinction. Also some conclusions derived from the project on the influence of extinction on chemical fires are presented.

An assessment of safety of the chemical storage facilities includes a brief discussion on the warehouse location, orientation and site access. The question of safety distances is handled in more details by presenting a four-step procedure as a guide to assess low risk distances. The ingredients of this procedure are 1) the survival fraction, 2) toxicity values, 3) fire scenario, dispersion and weather situation, and 4) the exposure time.

The approach and limitation of the models are presented emphasising the need to consider carefully the source strength, i.e. what fire scenario has been adapted.

[10] VTT Building Technology/ Fire Technology, P.O. Box 1803,FIN- 02044 VTT, Finland

6.2 An Engineering Approach to Fire Fighting Tactics

Lund [11] / Stefan Särdqvist

This project has the sub-heading *Elaborated Examples as a Basis for Guidelines for Fire Brigades at Fires in Chemical Warehouses*.

Faced with a rescue operation, the most important decision is whether to launch an offensive or a defensive operation. This part of the project presents a quantified model as a guide for the Incident Commander to determine the most suitable fire-fighting tactics in advance for given conditions at specific objects. This means to use an engineering approach to fire-fighting tactics.

The model proves that it is possible to introduce risk management procedures and fire safety engineering models into fire-fighting tactics. If the model and its different sub-models are improved and scientifically validated, fire brigades will gain a powerful tool for predicting their capacity.

The model consists of two parts. The first is the evaluation of the consequences of the fire, where the determination of the rate of heat release plays a central role, together with damage evaluation. The second is the determination of the extinction capacity of the fire brigade, or the rate of heat absorption. If the determined heat absorption is greater than the heat release, it is possible to launch an offensive operation. Otherwise, an offensive operation will fail to reach its aim, and a defensive approach is to be preferred, i.e. to direct all efforts into containing the fire within its boundaries. The concept is similar whether used before the fire, in a pre-planning situation, during the fire to analyse the situation, or after the fire for tactical evaluation.

This planning of intervention is part of the risk management process. During planning, some scenarios might show that an intervention is insufficient to reduce the consequences below the acceptance level. These cases should instead be managed by fire prevention measures.

The model proves that it is possible to introduce risk management procedures and fire safety engineering models into fire-fighting tactics, and that it is possible to determine suitable fire-fighting tactics in advance for a specific object under given conditions.

6.3 Tactical and operational structures in management of fires in chemical warehouses

NDC and FOA [12]/ Lars Fredholm

The report presents a conceptual framework concerning the tactical and operational problems and suggests procedures of analysis concerning four tactical problem situations to be applied on existing chemical warehouses. The purpose is that fire brigades in working with the conceptual structure and the procedures of analysis

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should be able to assimilate the results of the whole TOXFIRE project and prepare for fires in chemical warehouses.

The conceptual structure shapes a framework concerning tactical and operational management. A salient and important part of the framework is the structuring of tactical problem situations into four main categories, namely 1) a limited situation and strong resources, 2) a limited situation and critical resources, 3) a limited situation and weak resources and 4) an unlimited situation and weak resources. For each tactical category it is possible to define ”border setting” situations for existing chemical warehouses. A ”border setting” situation is a situation which constitutes the realistic possibilities for the fire brigade.

The report suggests for each category a procedure of analysis in order to prepare action concerning three main problem areas, namely 1) the fireground, 2) the operation as an operation with resources both from the fire brigade and the society outside the fire brigade and 3) the society outside the fireground. The intention is that an application of the conceptual structure and the suggested procedures of analysis on existing chemical warehouses should lead to an improvement of the co-ordinated competence in management of fires in chemical warehouses.

As the society outside the fireground is an important problem area, there is a discussion on problems to solve in relation to the people in the surroundings. The discussion concerns three summing up points of view. They are 1) that there is often more possibility for no reactions other than panic, 2) there is variation in the human behaviour in the impact area and 3) people need different types of information and possibilities to communicate with authorities, friends and relatives.

The idea of application of the conceptual structure and the suggested procedures of analysis is influenced by results from research on dynamic and distributed decision making. There you can find four general conditions in order to control any situation. They are 1) there must be a goal, 2) it must be possible to ascertain the state of the system, 3) it must be possible to affect the state of the system and 4) there must be a model of the system. The application of the framework and the suggested procedures of analysis is aimed at concretising these general conditions for each category of tactical problem situation.

6.4 Quick Decision System

VTT [13]/ Rhea Kakko

A warehouse fire may essentially be a structural and/or chemical fire.

When the chemicals are involved in the fire, e.g. explosions, vessel bursts, evolution of toxic vapours and/or aerosols may be the result. Cooling the fire area of chemical fires with water jets may increase the risks to the environment as the lower fire temperature may produce more toxic combustion products and the lower heat output makes the fire plume hug the ground. Massive water application may result in large

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amounts of polluted water which should not be allowed to flow into sewers or watercourses.

When arriving at the site, the fire officer must make quick decisions, which are currently based on the extinguishing plan of the object. However, the knowledge coming from case studies of warehouse fires emphasises that the fire officer needs also more information on the site/warehouse and the chemicals or products involved. The fire officer should also know the short and long term impacts of the decisions that he/she has made. When the direct and long term risks to humans are the main concern of the environmental impacts, the contamination must also be considered.

Large amount of detailed information is needed in the case of a chemical warehouse fire. The software developed in the project supports the collection of the preliminary information and tactics design and the fire officer's decision process during the fire. The software has been developed by VTT Manufacturing Technology. The expert knowledge and the instructions that form the basis of the software is compiled from the expert support group of the project including experts from the Finnish chemical industry and authorities, Finnish fire brigades, Finnish Rescue Institute, VTT Fire Technology and VTT Safety Engineering.

The software is designed for the Microsoft Windows environment. The main programming tool was ToolBook 4.0. The TOXDRAW target card drawing tool was programmed using Microsoft C++. The main goal of the software development was to make an interactive, easy-to-use application that supports the needs of the fire officer seeking information for their decision making.

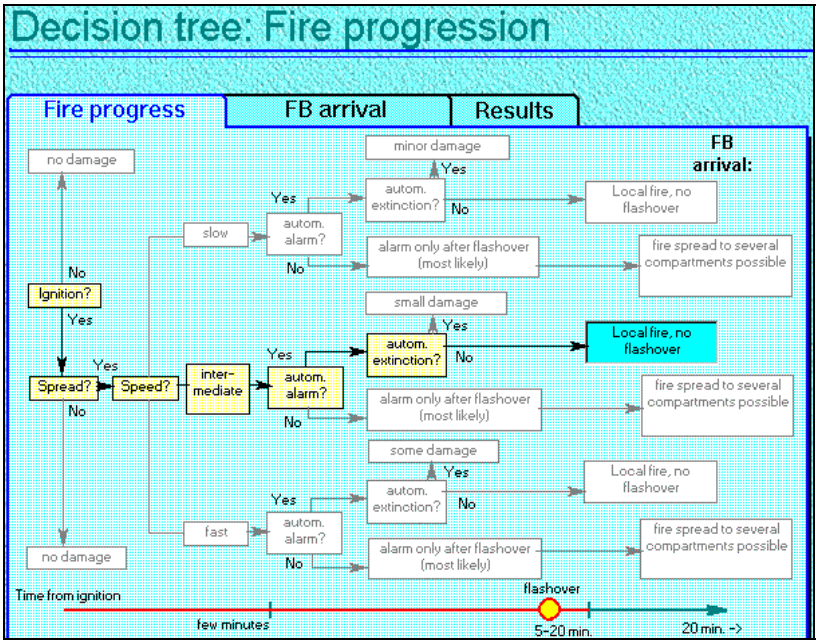

Figure 6 An example of the Decision Tree screen

The system is divided into four modes: Decision Tree, Reaction Matrix, Chemical Properties Database and Target Card Database. An example of the Decision Tree screen is presented in Figure 6.3.1. The TOXDRAW drawing tool is an additional tool, which can be linked to the system. Each module of the software has an unique decision support role in a fire situation, and combined, they form a powerful tool. The

software is now available in bi-lingual Finnish or English. The system was tested by Finnish fire brigades and the Finnish Rescue Institute.

The connection between fire inspection and emergency actions is essential when confronting hazardous chemical fires. Every decision system should support this link by transferring knowledge and/or maintaining information between inspection and action tasks. Many accidents can be prevented, if the fire officer together with the industry notices possible risks and prepare the emergency plans. If the fire officer also can predict the situation when arriving at the emergency scene, he/she can prepare the most efficient tactics to save human lives and protect the environment.

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Abstract (max. 2000 characters)

The report summarises the scientific outcome of the CEC Environment project "TOXFIRE. Guidelines for Management of Fires in Chemical Warehouses". The project was performed in the period 1994 - 1996 in a multi-national co-operation between partners from United Kingdom, Sweden, Finland and Denmark. The project included micro, small, medium, and two types of large scale combustion experiments. The experiments focused on the characterization of the combustion products and scaling effects are described. Additional, a few experiments on the effects of packaging and water on the fire products have been performed. Also included were items as fire modelling, risk assessment to human health and the environment. Finally, the basis of guidelines for safety engineers and fire brigades were established.

The report describes the work done by each partner and the main results achieved. The references of all reports from the TOXFIRE project are listed.

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