ASSESSMENT OF FIRES IN CHEMICAL WAREHOUSES:

A DESCRIPTION OF THE TOXFIRE PROJECT

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Abstract

The CEC Environment project "TOXFIRE. Guidelines for Management of Fires in Chemical Warehouses" was performed in the period 1994 - 1996 in a multi-national co-operation between partners from the United Kingdom, Sweden, Finland and Denmark. The project included combustion experiments, fire modelling, risk assessment to human health and the environment. Finally, the bases of guidelines for safety engineers and fire brigades were established and a quick decision system was developed.

Introduction

In many countries there is a large number of chemical plants and storage facilities that handle and store substantial amounts of hazardous substances. Chemical fires seem to be one of the most important hazards from these activities. The background for a number of projects funded by the European Commission is the recognition of a lack of knowledge e.g. on the generation of combustion products from stored agrochemicals after some major accidents which happened e.g. in Basle (Sandoz Fire) and in Nantes. 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:

- 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)

There are standardised test methods like the ISO-room to test room fires under almost real scale conditions. However, a warehouse is very much larger and therefore it is almost impossible to study such fires in real scale due to the extraordinarily high cost and the potential hazard for the people and the environment in the vicinity of such a test facility. Thus, in the case of warehouse fires an assessment needs some kind of modelling. Therefore, one of the important tasks in the TOXFIRE project was to compare different test methods and to describe the scaling effects. The advantages of a small scale[1] method are in general the low cost, fast achievement of test results and the fire products will not be harmful to the neighbourhood and the environment, as appropriate measures can be taken to prevent this. On the other hand the advantages of large scale methods are that the fire conditions are closer to the conditions of a real fire and it is believed that flame propagation and spread might only be tested in the large scale.

During the TOXFIRE project, which is partly based on the former COMBUSTION[2] project, five substances were chosen to be burned in all scale facilities. These are listed in Table 1 together with an example of the usage and the main expected toxic combustion gases. Important was the determination of survival fractions and a number of other characteristics of the substances like ignitability, heat release, burning rate, smoke evolution, combustion products and the influence of the packaging materials on the combustion products.

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. Further 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 is performed to develop 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 paper describes the overall objectives of the project and summarises the results obtained. A complete list of references to reports, articles and conference papers describing the experimental and modelling work is included in the final report [1].

Table 1: The five substances used in the scaling experiments

Substance	Example for usage	Expected combustion gasses
Polypropene *(PP $[C_3H_6]_n$)*	plastic (e.g. packaging)	carbon dioxide, carbon monoxide
Nylon 66 *(NY [C12H22N2O2]n)*	plastic (e.g. clothes)	hydrogen cyanide, nitrogen oxides
Tetrametylthiuram monosulfide *(TMTM C6H12N2S3)*	vulcaniser in rubber industry	sulphur dioxide, hydrogen cyanide, nitrogen oxides
4-Chloro-3-nitro-benzoic acid *(CNBA - C7H4NO4Cl)*	intermediate in dye production	hydrochloric acid, hydrogen cyanide, nitrogen oxides
Chlorobenzene *(CB C6H5Cl)*	solvent	hydrochloric acid

[1] small and large scale in this contents means amount of substances from a few gram to about 50 kg, respectively

[2] Combustion of Chemical Substances and the Impact on the Environment of the Fire Products; CEC STEP programme contract no. STEP CT91-0109

The structure of the project

In Figure 1 the structure of the TOXFIRE project is shown. As mentioned above there was an experimental part indicated as I, which objective was to establish data on combustion products including dioxin formation and to be able to assess scaling effects.

To be able to establish the basis of the guidelines (III), the data from the experiments and additional investigations (II) on fire spread (development of a nodal model) , assessment of human health effects on basis of data from pyrolysis experiments have been performed including effects due to fire suppression and ecotoxicological aspects.

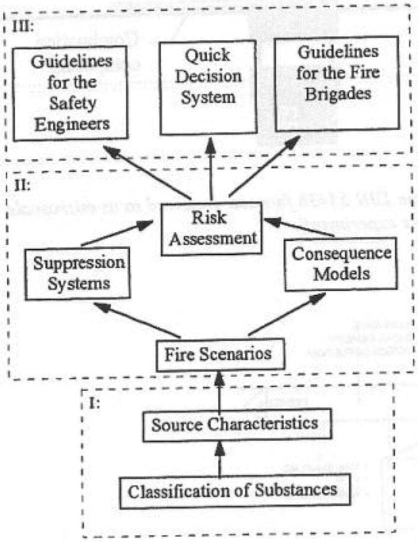

Figure 1. The structure of the TOXFIRE project.

In the initial phase of the project experiments have been made to screen for possible substances to be burned in all the scales. For this a flash pyrolysis setup [2] was chosen. Promising results have been obtained on the pyrolysis behaviour of the chemicals and the primary fuel. Furthermore, this method gave an upper limit for the survival fraction of the chemicals, as a flame consists of a pyrolysis zone in its core and a flaming region at the envelope of the flame where mainly the pyrolysis products react with oxygen. In the core of the flame the concentration of oxygen will be very low. Thus, when a substance is surviving the pyrolysis this is one of the conditions to be fulfilled to survive a fire. In this sense the flash pyrolysis results give an upper limit of the substances, which might survive in a pool fire.

The substances chosen to be burned in the micro scale (Figure 2), were mainly pesticides. The combustion products including dioxins have been analysed under different fire conditions. Additionally, the dioxin formation of two compounds has been measured in the small scale (Figure 3) and large scale ISO room (see Figure 5). The small scale experiments have been performed in a modified cone calorimeter which allowed for tests under oxygen deficient conditions. The medium scale experiments (Figure 4) have been performed under a variety of conditions on the five chosen and some additional reference substances. The large scale experiments have been performed on the five chosen substances. The extended large scale was performed to be able to make combustion tests on real storage configurations, e.g. the influence of packaging.

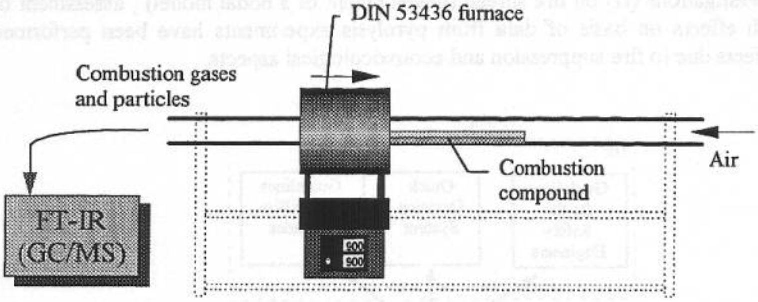

Figure 2. Setup of the DIN 53436 furnace. Referred to as microscale experiments (2 g of substance needed for one experiment).

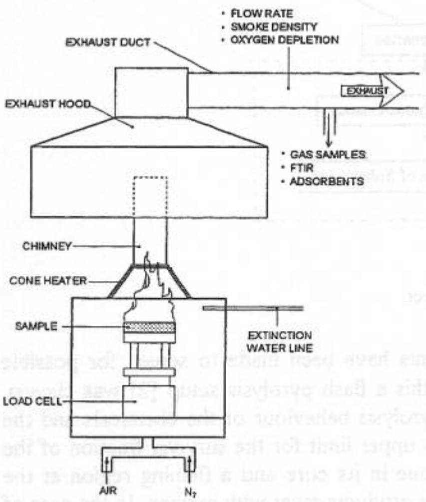

Figure 3. Setup of the cone calorimeter. Referred to as small scale experiments (20 g of substance needed for one experiment).

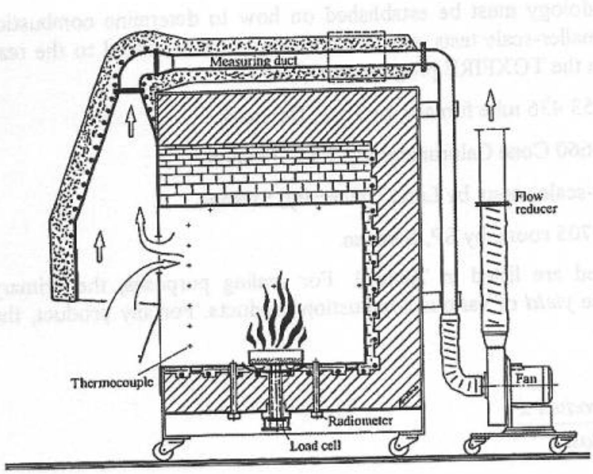

Figure 4. Setup of the 1/3 room scale facility. Referred to as medium scale experiments (1 kg of substance needed for one experiment).

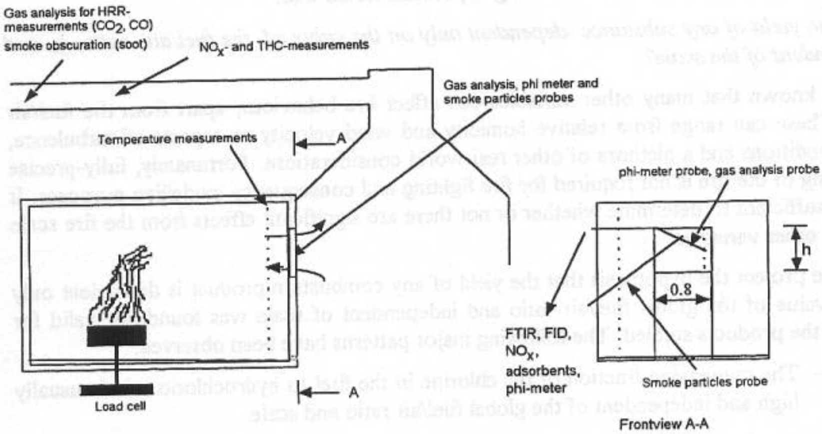

Figure 5. Setup of the ISO 9705 room facility, indicating the sampling probe configurations in the door opening and in the exhaust duct. Referred to as large scale experiments (50 kg of substance needed for one experiment).

The experimental results

A chemical warehouse fire is likely to occur in a building which is vastly larger than an ISO test room. Such fires are economically impossible to study in the real scale. Therefore, it is necessary to consider fire scaling in order to develop the proper fire fighting information. Thus, a methodology must be established on how to determine combustion properties on the basis of smaller-scale tests, which then have to be translated to the real-scale. The scales examined in the TOXFIRE program comprise:

- Micro scale. DIN 53 436 tube furnace, by Risø, Denmark.
- Small scale. ISO 5660 Cone Calorimeter, by VTT, Finland.
- Medium scale. 1/3-scale room, by Lund University, Sweden.
- Large scale. ISO 9705 room, by SP, Sweden.

The five chemicals studied are listed in Table 1. 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 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 sufficient 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 combustion product is dependent only on the value of the global fuel/air ratio and independent of scale was found not valid for most of the products studied. The following major patterns have been observed:

- The conversion fraction of the chlorine in the fuel to hydrochloric acid is usually high and independent of the global fuel/air ratio and scale.
- 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 (see Table 2).

Table 2 Results of scaling experiments in yields of ng I-TEQ / g substance (indicates extinction with water).*

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

The results of dioxin formation in micro, small and large scale at various temperatures and loads are listed in Table 2. It is seen that the results for the micro and large scale are comparable with the same temperature dependency indicating the absence of major scaling effects. Surprisingly, the small scale cone calorimeter results are somewhat higher, and the influence of the temperature is the opposite as of the other experiments.

Basis of guidelines

Based on the results of the TOXFIRE items and available literature it was tried to develop the basis of guidelines for the safety engineers to prevent fire incidents by proper construction and basis of guidelines for the fire brigades to prepare themselves for emergency situations.

The the guidelines for safety engineers is based on the methodology described in the literature, e.g. ISO/TC 92/SC4 "Fire Safety Engineering" documents and on the findings from the project. This is described by VTT [3] and basic elements of fire safety design of a chemical warehouse like construction design (compartmentation and structures, escape routes, smoke ventilation and retention of spills and fire fighting water), model fires and fire simulation, storage and packaging, preventive and protective systems, building location and safety distances are discussed. In particular, the influences of storage layout and packaging on fire spread and the consequences of fire are discussed, including the effects of

- the size and separation of the stacks
- the physical properties of the packaging
- the nature of the stored materials
- the mechanisms in which packaging can contribute to the fire.

Effects of fire extinction are mentioned and the question of safety distances is discussed more detailed by suggesting a four-step procedure as a guide to assess such distances. The steps are requiring information on the

- survival fraction
- toxicity values
- fire scenario, dispersion and weather situation
- exposure time.

The basis of the guidelines for the fire brigades is described in two reports [4, 5] from Lund and FOA. Both are dealing with fire fighting tactics and Lund is discussing the possibilities to introduce risk management procedures and fire safety engineering models into fire fighting tactics. The approach is divided into two parts.

- The first part is about the evaluation of the consequences of a fire. Here the determination of the rate of heat release is very central in combination with the damage evaluation.
- The second part is about determination of the extinction capacity of the fire brigade, or in other terms the rate of heat absorption.

For the appropriate fire fighting tactics this means that 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. The concept is similar for different purposes, as it can be 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 interventions 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. Thus such 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.

FOA is describing a conceptual framework concerning the tactical and operational problems and suggest procedures of analysis concerning four tactical problem situations to be applied on existing chemical warehouses. These tactical problem situations are

- a limited situation and strong resources
- a limited situation and critical resources
- a limited situation and weak resources
- an unlimited situation and weak resources

For each tactical category it is possible to define "border setting" situations for existing chemical warehouses. Border setting should be understood as a situation which constitutes the realistic possibilities for the fire brigade. For each category a procedure is suggested in order to prepare action concerning three main problem areas

1. the fireground

2. the operation as an operation with resources both from the fire brigade and the society outside the fire brigade
3. the society outside the fireground.

Also a quick decision system [6] was established by VTT as an EDB based program to be used in emergency situations. The system is divided into four modes: decision tree, reaction matrix, chemical properties database and target card database. The TOXDRAW target card drawing tool can be linked to the system. This is due to the main goal of the software development to make it an interactive, easy-to-use application that supports the information needs of the fire officer in the decision making process. Therefore, the software supports the collection of the preliminary information from inspections at the sides and the tactics design for the fire officer to be prepared in the emergency situation. This system has been tested by the Finnish firebrigade and the Finnish rescue institute and will be further developed after the first positive feedback.

Conclusion

The TOXFIRE project gave many encouraging results, which can be used to improve estimation of emissions from the building under different situations / phases of a fire. Hopefully, the information and methods are useful for safety engineers in the planning phase, for the fire brigades in preparing for emergency situations and also in the emergency situation as well.

Acknowledgements

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