

TNO-report

Toxic combustion products from pesticide fires
Executive summary

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Summary

In order to obtain reliable data on the generation of toxic combustion products and to get more insight into the risks of fires in pesticide warehouses TNO performed the research project 'Toxic combustion products from pesticide fires'. The following research activities have been performed during the project:

- A study of the casuistry of pesticide fires;
- A literature study of small scale combustion test methods;
- Execution of medium scale combustion experiments with pesticides;
- A study on the extrapolation of the emissions of small and medium scale combustion tests to real fire conditions;
- A study on the prevention and control of fires in pesticide storages.

Most important results and conclusions of the project.

- The medium scale combustion experiments with parathion, chlorfenvinphos, dichlobenil and 2,4-D indicate the following:
 - Emissions of solids (particles and soot), carbon monoxide and hydrocarbons are higher than assumed in present hazard assessment studies;
 - Emissions of nitrogen oxides and chlorinated dioxins and furans are lower than assumed in present hazard assessment studies;
 - Chlorine and sulphur in the pesticide are nearly fully converted into hydrogen chloride and sulphur dioxide;
 - The emissions of ammonia, chlorine and phosgene are below or just above detection limits;
 - Large quantities of solid residues remain in all fires. The residues contain up to 10% unburnt pesticide;
 - Simulated fire extinguishing or oxygen deficiency do not significantly influence the emissions during the medium scale experiments.
- Similarity requirements to extrapolate the emissions to pesticides other than those investigated have been determined. As these similarity requirements will not be completely fulfilled in many cases the uncertainties in the extrapolated emissions are large.
- The following conservative conversion rates are proposed for a pesticide fire:

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Component	Conversion rate		
CO	14	%	of the carbon in the pesticide
C _x H _y	3.5	%	of the carbon in the pesticide
NO _x	25	%	of the nitrogen in the pesticide
HCN	3.8	%	of the nitrogen in the pesticide
SO ₂	100	%	of the sulphur in the pesticide
HCl	100	%	of the chlorine in the pesticide
PCDD/F (TEQ)	36.10 ⁻⁷	%	of a chlorinated aromatic pesticide
Solids (soot)	16	%	of the pesticide
Pesticide	0.57	%	of the pesticide
Solid residue	32	%	of the pesticide
Residual pesticide	2.6	%	of the pesticide

Fire protection systems

- A methodology has been developed to define the required fire protection level of a pesticide storage:
 - The required fire protection level for a pesticide storage depends on the product fire hazard, the packaging fire hazard, and the environmental and health hazard of the stored materials;
 - Four fire protection levels for a pesticide storage are distinguished in the methodology, with fire protection levels having different requirements. For level one only the basic minimum requirements like good facility lay out, ignition source control, good housekeeping and regular training of employees are necessary. The highest protection level is level four. For level four automatic fire alarms, sprinkler systems and a basin for extinguishing water are additional requirements.
- Application of this methodology is recommended to obtain a cost effective protection level for a pesticide storage taking into account the hazards of the stored pesticides.

Small scale test methods

- Based on the results of the study on the characteristics of small scale test methods it can be concluded that the applicability of small scale test methods to predict the emission of toxic products of a pesticide fire is very limited.
- Small scale methods should be further developed in order to improve the simulation of the fire conditions observed during the medium scale experiments.

Case histories

- Due to the very general description of the case histories it was impossible to get reliable data on the causes, development and consequences of pesticide fires.

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Figure 1 Schematic of experimental combustion facility

Figure 2 Schematic of measuring and sampling equipment

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1 Introduction

Pesticides are stored in warehouses. Although most pesticides are used in formulations with a relatively low percentage of active material, the stored products may have hazardous properties. Especially in the case of a fire specific hazards may exist. The hazards of a pesticide fire are the possible release of pesticides because of damage of packagings, and the generation and emission of toxic combustion products. Released pesticides and combustion products will pollute the environment via dispersion into the atmosphere and via the fire fighting water.

In 1978 TNO started research in the field of hazard assessment of pesticide storages. The objective of this research was to develop an hazard assessment methodology for pesticide storages. One of the greatest uncertainties in the hazard assessment methodology concerned the generation rate of toxic combustion products in a pesticide fire. A comprehensive literature search has been executed on the subject of generation of toxic combustion products in fires. From the literature search it was concluded that reliable quantitative data on the generation rate of toxic combustion products was not available. Therefore conservative assumptions with respect to the generation of toxic combustion products were made when assessing the hazards of a fire.

In order to obtain reliable data on the generation of toxic combustion products and to get more insight into the risks of fires in pesticide warehouses TNO issued the research proposal 'Toxic combustion products from pesticide fires'. The project was set up to gain clear insight into:

- The usefulness of results obtained with small scale combustion test methods to predict emissions of pesticide fires;
- The generation of toxic products during uncontrolled combustion of different chemical categories of pesticides;
- The influence of the combustion conditions of fires on the emission of products;
- The possibilities of scaling pesticide fires;
- The most desirable preventive and control strategies with regard to pesticide fires.

The following research activities have been performed:

- A study of the casuistry of pesticide fires;
- A literature study of small scale combustion test methods;
- Execution of medium scale combustion experiments with pesticides;
- A study on the extrapolation of the emissions of small and medium scale combustion test to real fire conditions;
- A study on the prevention and control of fires in pesticide storages.

This summary report presents the results of the project. A comprehensive description of all research activities is presented in five reports of which the titles are given in chapter 8 of this executive summary.

The project was executed by the TNO Institute of Environmental and Energy Technology and coordinated by the Department of Industrial Safety. The

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Department of Combustion Technology and the Department of Analytical Chemistry participated in the project. The project has been executed from 1988 till 1991 and was sponsored by:

- Enichem Agricoltura, Italy;
- Joint Research Centre of the European Communities (JRC Ispra), Italy;
- Ministry for Home Affairs, Fire Services Inspectorate, The Netherlands;
- Ministry of Housing, Physical Planning and Environment, The Netherlands;
- Ministry of Social Affairs, Labour Inspectorate, The Netherlands;
- Rhône-Poulenc, France;
- Shell Internationale Chemie Maatschappij B.V., The Netherlands;
- Solvay Duphar B.V., The Netherlands;
- TNO, The Netherlands.

The execution of the research activities, the selection of the pesticides for the combustion experiments, the progress and final reports were discussed with the Steering Committee. The Steering Committee was composed of the following representatives:

Mr. Picardi / G. Camaggi, Enichem Agricoltura;
Mr. G. Mutzbauer, JRC Ispra;
Mr. W. Klijn / Mr. H. Mugie, Fire Services Inspectorate;
Mr. R.O.M. van Loo, Ministry of Housing, Physical Planning and Environment;
Mr. H.O. van der Kooi, Labour Inspectorate;
Mr. R. Dubus / Mr. J. Ph. Lopez, Rhône-Poulenc;
Mr. R.J.C. van Leth / Mr. D. Zwartbol, Shell;
Mr. G. van Buuren, Solvay Duphar.

The Steering Committee had four meetings. The discussions with the Steering Committee were very fruitful and contributed to gain the desired project results. Particularly the expertise of the members of the Steering Committee with respect to physical, chemical and toxicological properties, handling and storage of pesticides and regulations concerning pesticides were of great value to the project. It is acknowledged that this project only could be executed with the support of the members of the Steering Committee and the financial contribution of the Sponsors.

2 Analysis of case histories of pesticide fires

The aim of the analysis of case histories of pesticide fires was to obtain data on the causes, development and consequences of fires in pesticide storages. A search in the literature and accident data bases has been executed to find case histories of pesticide fires in depots and production plants. In total 12 fires in pesticide warehouses and 13 pesticide fires in chemical plants have been found.

The case histories of the warehouse fires were very general. Details with respect to the construction of the warehouses, the fire safety, the way of storage and the stored materials were not given. Analyses of the causes of the fires are generally not given in the case histories. Therefore it was not possible to get reliable data on the causes, development and consequences of the fires. Some conclusions are:

- In general the warehouses involved in the fires were not equipped with automatic fire detectors and alarms or with (automatic) sprinkler systems;
- Friction heat or overheating, hot works and nearby fires are often causes of fires in pesticide storages;
- The consequences of the fires are water and soil pollution and injuries due to inhalation of toxic fumes. In the majority of cases only firemen and employees were injured. Residents were sometimes affected by the toxic fumes, but after a short treatment in hospital they recovered.

3 Small scale combustion test methods

During the project more than 25 laboratory pesticide combustion methods have been evaluated. These methods allow to burn pesticides on a 1 g/h scale. It was concluded that none of the methods can be generally accepted as a good method producing high quality data on toxic combustion products from pesticide fires. For this two reasons can be mentioned:

- The conditions in a real fire will deviate largely from the conditions in a laboratory system;
- No experimental data are available to validate the laboratory methods.

During the combustion process the following stages can be distinguished: drying, melting, boiling, volatilization, thermal degradation, gas phase combustion and combustion of the carbon residue. For complete combustion sufficient oxygen should be available, the temperature should be high enough and the residence time in the flame should be sufficiently long. These conditions are not satisfied in an uncontrolled fire and incomplete combustion will occur. This will result in emissions of unburnt (chlorinated) hydrocarbons, partially oxidized materials and unburnt particles, like soot. A perfect laboratory method should be able to simulate all these conditions simultaneously.

Best suited to simulate fires seem to be the Casf-method, Tewarson-method and Ciba Geigy-method. Presently no reliable data are available to validate these methods.

4 Medium scale combustion experiments with pesticides

The objective of the medium scale combustion experiments was to obtain reliable data on the emission of toxic products during an uncontrolled fire. It was decided to perform experiments on a medium scale because the small scale test methods do not simulate real fire conditions. Moreover sampling of flue gases of large scale experiments is difficult, the conditions are often not reproducible and large scale experiments are very expensive. It was expected that the medium scale experiments could be used to define the conditions which are important in a fire and should be simulated in a small scale test.

4.1 Pesticides selection criteria

The following considerations were applied to select the pesticides for the experiments:

- The pesticides should have a high market volume;
- Very toxic pesticides ($LD_{50, oral} \leq 25$ mg/kg) should be included, the emission of unburnt pesticides in a fire can be a significant hazard;
- The selected pesticides should have N, Cl or S in the molecular structure in order to investigate the generation of the acute toxic compounds: nitrogen oxides, hydrogen chloride and sulphur dioxide and the generation of hydrogen cyanide, ammonia, chlorine, phosgene and hydrogen sulphide;
- Chlorinated aromatic hydrocarbons should be included to investigate the generation of chlorinated dioxins and furans;
- Liquid and solid pesticides should be included to investigate the influence of the physical state on the emissions;
- Generally pesticides are formulated with solvents, water or inert solids and other additives. A lot of commercial solvents and additives are applied that probably will influence the combustion process and the emissions. Mainly (technical) pure pesticides should be tested to exclude these unknown influences.

4.2 Tested pesticides

Application of these criteria led to the selection of the following pesticides for the combustion experiments:

- Parathion (liquid organophosphate, very toxic, containing N and S);
- Chlorfenvinphos (liquid organophosphate, very toxic, containing Cl);
- Dichlobenil (solid aromatic hydrocarbon, containing N and Cl);
- 2,4-D (solid aromatic hydrocarbon, containing Cl; liquid compounds).

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4.3 Combustion facility

A special experimental combustion facility with a flue gas sampling system has been developed and constructed for the combustion experiments. In this combustion facility liquid and solid pesticides can be burnt on a burner plate in a free burning flame on a 1 kg/h scale. The burner plate can be heated electrically or by a natural gas burner to ignite the pesticide and/or to maintain the fire. In the furnace room facilities to reduce the combustion air supply can be installed to simulate pyrolytic combustion. A water nozzle to simulate fire fighting with water can be used. Figure 1 presents a scheme of the combustion facility.

Flame temperatures at different positions in the fire and heat flux densities can be measured. The flue gas sampling system is composed of several sub-systems to sample for solid particles, macro-components (like O₂, CO₂, CO, SO₂, NO_x, C_xH_y, HCl) and microcomponents (like pesticides, Cl₂, COCl₂, H₂S, HCN, chlorinated dioxins and furans). A schematic of measuring and sampling equipment is given in figure 2.

4.4 Combustion experiments

Three combustion experiments with different burning conditions have been executed with parathion and chlofenvinphos. The first experiment for each pesticide was with normal air supply and no fire extinguishing, the combustion air supply was reduced during the second experiment and fire extinguishing was simulated during the third experiment. Five dichlobenil experiments with normal air supply without extinguishing, with water extinguishing, with extra heat input, with double pesticide input and with natural gas afterburning of flue gases respectively were executed. For all conditions the fire temperatures and the emissions of combustion products did not vary significantly. Finally it was decided to investigate whether a higher flame temperature would influence the emissions. For the 2,4-D experiments the composition of the 2,4-D was varied by the addition of an organic solvent to increase flame temperature. The combustion experiments were executed with technical 2,4-D (≈ 100% 2,4-D), 2,4-D ester (66.3% 2,4-D) and a mixture of 2,4-D ester and kerosine (49.4% 2,4-D). Blank experiments have been executed to determine background levels of the sampled components in ambient air, in flue gases from natural gas and in the combustion facility and sampling system.

4.5 Experimental results

During the combustion experiments the pesticides burn like in a fire. In general the flame temperatures were very low. The maximum observed flame temperature was below 700 °C at 0.15 m above the burner table, at 0.30 m above the burner table the observed flame temperature was less than 500 °C. Reduced combustion air supply and water extinguishing did not influence the flame temperatures significantly. The average observed flame temperatures during the

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fires of the 2,4-D mixtures with kerosine were approximately 100 °C higher than during the other fires.

The results of the flue gas analyses are presented in table 1. In the table no distinction is made for the fire conditions (normal air supply, reduced air supply and water extinguishing) as there is no significant effect of the different conditions on the emissions.

Table 1 Emissions of medium scale (1 kg/h) pesticide fires

Component	Emission factors (g/kg pesticide)							
	Parathion		Chlorfenvinphos		Dichlobenil		2,4-D-compound	
CO	49	- 62	45	- 132	52	- 106	49	- 65
C _x H _y	1	- 10	5.7	- 18.6	0	- 3.2	12.2	- 21.7
NO _x	2	- 4		0	1.7	- 4.3	0	- 2.3
NH ₃	0	- <0.0006			<0.00014	- <0.00017		
HCN	0.7	- 0.9			2.8	- 5.9		
SO ₂	119	- 133						
H ₂ S	0.006	- 0.07						
HCl			162	- 202	150	- 262	137	- 182
Cl ₂			<0.005	- <0.013	0.17	- 0.24	<0.088	- <0.321
COCl ₂			0.006	- 0.013	0.00052	- 0.00063	<0.042	- <0.053
PCDD/F (in TEQ)				- <12.10 ⁻⁶		- <0.26*10 ⁻⁶	4*10 ⁻⁶	- 36.10 ⁻⁶
Solids	85	- 116	99	- 157	51	- 57	37	- 85
Parathion	0.8	- 4.4						
Chlorfenvinphos			0.02	- 0.6				
Dichlobenil					4.3	- 5.7		
2,4-D							0.00271	- 1.01
Solid residue	242	- 319	121	- 302	70	- 70	12	- 37
Residual parathion	0.7	- 26						
Residual chlorfenvinphos			0.002	- 0.019				
Residual dichlobenil					1.2	- 6.5		
Residual 2,4-D							0.00073	- 0.124

4.6 Discussion

The observed maximum flame temperatures of a medium scale pesticide fire are lower than 700 °C. Due to the low temperatures large quantities of solids (particles and soot) and carbon monoxide are formed in the root of the pesticide fire. The temperature is too low for subsequent complete combustion of solids, carbon monoxide and other products of incomplete combustion. Therefore the emissions of carbon monoxide (about 10% of the carbon input) and solids (about 10% of pesticide input) are relatively high. Also a large quantity (about 2% of carbon input) of hydrocarbons is emitted. The temperatures of the fires of the 2,4-D compounds with hydrocarbons are approximately 100 °C higher. The effect is a smaller emission of carbon monoxide and solids.

Probably due to poor combustion conditions (low oxygen availability in the flame, low flame temperatures) the emissions of nitrogen oxides are low; less than 2.4% of the nitrogen in the pesticide is converted into NO_x. The emission of

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ammonia can be neglected. For dichlobenil the emission of hydrogen cyanide is ≤ 5.9 g/kg pesticide.

The emission of sulphur dioxide equals about 60% of the maximum value for complete conversion of S into SO₂. The hydrogen sulphide emission is very low; less than 0.06% of the sulphur in the pesticide is converted into H₂S.

The hydrogen chloride emission equals 40 - 85% of the value for complete conversion of Cl into HCl. The emissions of chlorine and phosgene are below or slightly above detection limits and can be neglected. The emissions of chlorinated dioxins and furans are for the chlorfenvinphos and dichlobenil fires below the detection limit, for the 2,4-D fires they are slightly above the detection limit.

The emission of unburnt pesticide is lower than 1% and lowest for 2,4-D. This can be caused by the higher temperatures during the 2,4-D fires. Large quantities of solid residue remain after all fires. The residues contain less than 10% pesticide.

From the experiments it is concluded that in a medium scale pesticide fire the combustion is far from complete due to low flame temperatures. For a small scale test it is important to simulate these conditions. It should be investigated whether the conversion rates into toxic products determined during this project are also valid for a fire of chemicals at higher temperatures.

5 Scaling of pesticide fires

The objective of the study on the scaling of pesticide fires is to answer the following questions:

- Is it possible to extrapolate emission factors from intermediate scale (≈ 1 kg/h) fires to emission factors for real fires (≈ 1000 kg/h);
- Is it possible to extrapolate emission factors from small scale (≈ 1 g/h) fires to emission factors for real fires (≈ 1000 kg/h)

5.1 Similarity requirements

Combustion may be scaled from one process to another process if the combustion processes are similar. Similar pesticide fires occur if the distribution of residence times, temperatures, oxygen and pesticide concentrations and the chemical reactions are similar.

In order to establish scaling rules for the emissions of a pesticide fire, simultaneous similarity is required in the following areas:

- Similarity of pesticide to obtain the same chemical reactions;
- Geometric similarity with dimensions of fires proportional both with respect to boundaries and internal geometry like flame shape;
- Kinematic similarity with similar aerodynamic (flow)/mixing patterns;
- Thermal similarity with similar thermal processes (heat release, heat transfer, temperature distributions).

These similarity requirements can only be fulfilled simultaneously if the pesticide fires are completely identical. In reality this will never occur. For drawing up scaling rules some of the above mentioned similarity requirements will be violated and this causes an uncertainty in the scaling process.

5.2 Theoretical scaling rules

The main part of combustion scaling research in literature relates to the combustion of fossil fuels and hazardous waste incineration. In practice scaling of burner/furnace systems is limited to a factor of 10 and preferably to a smaller factor.

Conclusions from the theory of fire scaling are:

- If pesticides are stored on pallets on the floor (with height small compared to length or width) the pesticide combustion rate per area is constant;
- If pesticides are stored in racks or palletized piles the pesticide combustion rate per area increases with the square root of the main storage dimension (e.g. height);
- If air supply is limited the burning rate can be calculated from the oxygen availability;
- Residence times in a fire will increase if the fire becomes larger;

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- Temperature levels in large scale fires will be higher than in small scale fires;
- If residence times and temperature levels increase with fire size and if air can freely enter the fire it is expected that combustion will be more complete for larger fires; for pesticide fires this means that less pesticides will be emitted and more combustion end products, like CO₂, H₂O, NO_x, SO₂ and HCl, will be produced.

5.3 Test methods

Small scale test methods

The evaluated existing small scale test methods are not a realistic simulation of a large scale fire and rules to scale a small scale fire (1 g/h) to large scale (1000 kg/h) have not yet been developed. Small scale methods which better simulate the real fire conditions should be developed and tested in order to quantify toxic combustion products from pesticide fires.

Medium scale test methods

Emission factors determined during the present project (medium scale of 1 kg/h) can be extrapolated to a pesticide pool fire or a fire of pesticides stored in racks or in piled pallets.

Application of the theoretical scaling rules leads to the following conclusions:

- Within a certain degree of uncertainty it is expected that emissions per kilogram burnt pesticides of toxic products due to a large scale fire are the same or lower than in the medium scale test;
- For a large scale pesticide fires with restricted air supply the emission of products of incomplete combustion (e.g. CO, C_xH_y, HCN, H₂S) will be higher than during medium scale tests.

A possible exception to these extrapolation rules is the emission of NO_x. During the executed medium scale experiments the temperatures and oxygen availability were low, probably resulting in low NO_x emissions. It may be expected that a pesticide fire with better combustion conditions will have higher NO_x emissions.

5.4 Fires of other pesticides

Emission factors for a fire of a pesticide may be used for a second pesticide if:

- The calorific value of the second pesticide is the higher one;
- The calorific value of any constituent of the second pesticide is higher than that of the first pesticide;
- The contents of chlorine, nitrogen, phosphorus, sulphur and ash in the second pesticide are lower than in the first pesticide.

The emission factors of CO, solids, pesticide and solid residue during the medium scale combustion experiments, that meet the similarity requirements, fulfil the

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extrapolation rules. For other components the picture is less clear. In order to establish emission factors for all components from other pesticides that do not fulfil the similarity requirements the following approach is suggested:

- The emission factor for a component equals the maximum emission factor measured during the experiments;
- For NO_x a conversion rate of 25% of the nitrogen in the pesticide is suggested; this figure is at the lower end of conversion rates from fossil fuel combustion;
- For SO₂ and HCl it is assumed that complete conversion of pesticide S and Cl will occur.

These considerations lead to the following emissions for a pesticide fire. As the similarity rules most times will not be fulfilled the uncertainty in these conversion rates may be quite large.

Table 2 Conversion rates into combustion products for a pesticide fire

Component	Conversion rate		
CO	14	%	of the carbon in the pesticide
C _x H _y	3.5	%	of the carbon in the pesticide
NO _x	25	%	of the nitrogen in the pesticide
HCN	3.8	%	of the nitrogen in the pesticide
SO ₂	100	%	of the sulphur in the pesticide
HCl	100	%	of the chlorine in the pesticide
PCDD/F (TEQ)	36.10 ⁻⁷	%	of a chlorinated aromatic pesticide
Solids (soot)	16	%	of the pesticide
Pesticide	0.57	%	of the pesticide
Solid residue	32	%	of the pesticide
Residual pesticide	2.6	%	of the pesticide

6 Prevention and control of fires in pesticide storages

The aim of this subproject was to develop a fire prevention and fire fighting approach that is suited for pesticide storages, taking into account the stored materials, the properties of the building and the fire protection measures taken.

Based on the theoretical aspects of fire generation and fire development and on the fire properties of the storage facilities and stored materials a methodology has been developed for assessing the proper fire protection levels. These levels correspond to a number of fire protection requirements, including fire detection and fighting systems and compartmenting and containment facilities.

6.1 Fire properties of storage facilities

The fire safety of a storage facility is in part determined by the design and lay-out of the warehouses and office buildings. A storage facility must have good accessibility for the fire brigade and rescue teams. Water supply must be assured. Measures to prevent unwanted visitors from entering the premises will decrease the probability of arson.

Inside warehouses the arrangement of stores is important. Solid piling of the pesticide gives the lowest opportunity for fire development. However if the outer surfaces possess rapid flame spread properties, high stacks may form a severe hazard. Pallets provide horizontal air spaces which are often out of reach of sprinkler heads. In racks not only horizontal but also vertical air spaces may exist. Air spaces will always contribute to fire spread.

In designing a construction the number of weak spots must be minimized. Interruptions of fire resistant walls or roofs must be avoided as much as possible. Application of fire resistant layers or coatings may greatly enhance the fire resistance. Vulnerable parts of a construction are any connections between walls, floors, roofs, etc. and parts built up with poor fire properties. The best construction materials to be used are the ones which combine low flammability with remaining strength during a fire (concrete, masonry/brick, and the heavier wooden constructions).

6.2 Fire detection and fire fighting systems

Automatic fire detectors operate according to principals of thermal detection, smoke detection, gas sensing fire detection and flame detection. The response time of the latter is long. In storages preferably fast response detection systems must be applied.

Automatic fire fighting systems are sprinkler installations, water spray fixed systems ('deluge'), foam-water spray systems and foam-water sprinkler systems,

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and dry chemical extinguishment systems. Because of practical reasons water and water foam extinguishing systems are most appropriate in pesticide storages.

If the fire has to be extinguished by a fire brigade a distinction is made between a quickly responding and fully operational fire brigade ('category 1 fire brigade') and a 'category 2 fire brigade' (which does not meet the requirements of the category 1 brigade).

In case of heavy smoke formation ventilation may be considered. The main reasons are:

- Saving lives of people present in the building;
- Provide better visibility for the fire fighters;
- Prevent smoke explosions;
- Control the spread of the fire, by exhausting hot fumes.

In a pesticide storage it is not very likely that many people are inside the building. The visibility inside a storage may already be poor due to high piles of stored products. In such a case it is questionable whether smoke ventilation will greatly improve visibility. The conditions during a fire in a storage and the materials involved are not such that flash-over is very probable. And finally the spread of the fire will be dominated by the availability of flammable products and packages in the storage.

6.3 Required fire protection level of a pesticide storage

In order to establish the appropriate fire safety measures in a storage a methodology has been developed which is based on four so called fire protection levels, numbered with increasing protection from I to IV. The levels are dependent on the product fire hazard, the packaging fire hazard, and the environmental and health hazard. The fire protection requirements that belong to each of the fire protection levels consist of a number of basic requirements, requirements regarding fire detection and fire fighting systems, and requirements concerning compartmenting and containment facilities.

The basic requirements are:

- A good facility lay-out, good accessibility of the site for the fire brigade;
- Ignition source control: no smoking, hot work only with a proper license, proper maintenance of the electrical installation, no other equipment generating sparks, open flames or shrink-wrapping equipment operated in the storage;
- Good housekeeping, rotation of stores, regular maintenance of stores;
- Regular training of employees, instruction of visitors, labelling and signing of potentially hazardous situations;
- Local fire brigade.

The minimum requirements for the four protection levels are given in table 3.

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Table 3 Minimum fire fighting requirements in relation to the protection levels
(X means required)

Requirements	Fire protection levels						
	I	IIa	IIb	IIIa	IIIb	IVa	IVb
Basic requirements	x	x	x	x	x	x	x
Local fire brigade	x	x	x	x	x	x	x
Fire detection system	-	x	x	x	x	x	x
Company (category 2) fire brigade	-	-	-	x	x	-	-
Manual or semi-automated extinguishing system	-	-	-	x	x	-	-
Automated extinguishing system	-	-	-	-	-	x	x
Fire water containment facility	-	-	x	-	x	-	x

The required fire protection level for a pesticide storage depends on the product fire hazard, the packaging fire hazard, and the environmental and health hazard of the stored materials. Based on these data, the fire protection level can be determined according to table 4.

Table 4 Fire protection levels (I-IV) as determined by the product fire hazard category (FH), the packaging (flammable/non flammable) and the environmental and/or toxic hazard (E, T, ET, O)

Fire hazard categories			Environmental and/or toxic hazards		
category	criteria	packaging	E, ET	T	O
FH 1	- flammable liquids; flash point <55 °C - flammable gases - materials that generate flammable gases after contact with water - explosive materials - oxidizing materials	flammable, non flammable	IVb	IVa	II
FH 2	- flammable liquids; flash point 55-100 °C - flammable solids with low ignition temperatures	flammable non flammable	IVb IIIb	IVa IIIa	II II
FH 3	- liquids with flashpoint >100 °C - flammable solids with high ignition temperatures	flammable non flammable	IIIb IIb	IIIa IIa	I I
FH 4	- non-flammable solids and liquids	flammable non flammable	IIb I	IIa I	I I

E environmental hazard ($LC_{50}(\text{fish}, 96 \text{ h}) \leq 1 \text{ mg/l}$)

T very toxic to man ($LD_{50}(\text{oral}, \text{rat}) \leq 25 \text{ mg/kg}$)

ET environmental hazard as well as (very) toxic to man

O no environmental or toxic hazards

7 Conclusions and recommendations

The project 'Toxic combustion products from pesticide fires' aimed to obtain an insight into:

- The usefulness of results obtained with small scale combustion test methods to predict emissions of pesticide fires;
- The generation of toxic products during uncontrolled combustion of different chemical categories of pesticides;
- The influence of the combustion conditions of fires on the emission of (toxic) products;
- The possibilities of scaling pesticide fires;
- Desirable preventive and control strategies with regard to pesticide fires.

From the results of the project the following lessons can be learnt.

Applicability of small scale tests

Results

Based on the results of the study on the characteristics of small scale test methods and the medium scale combustion experiments it can be concluded that applicability of small scale test methods to predict the toxic products of a pesticide fire is very limited. The Casf, Tewarson and Ciba-Geigy method are best suited to simulate practical fires. However the conditions in these methods differ from the conditions in a fire.

Recommendations

The small scale methods should be further developed and tested to proof that fire conditions as observed during the medium scale experiments are simulated better. Another option is to test not all pesticides in a small scale method, but to test more pesticides in a medium scale test method. Based on the results of these medium scale experiments and the properties of the pesticide (calorific value, molecular structure, etc.) conversion rates into toxic combustion products for a pesticide fire could be extrapolated.

Generation of toxic products during a pesticide fire

Results

During the project four pesticides have been burnt in the medium scale combustion facility. Some experiments have been executed with obstructed combustion air flow and with fire extinguishing.

In general the measured emissions of toxic combustion products are lower than generally assumed, except for the emission of carbon monoxide and solids (particles and soot). These emissions can be explained by the low flame temperatures (< 700 °C) in the medium scale pesticide fires.

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The opinion that chlorinated dioxins and furans will be generated in a fire of pesticides is not confirmed by the results of the experiments. The emissions of chlorinated dioxins and furans are below the detection limit for the chlorfenvinphos and dichlobenil fires. For the 2,4-D fires emissions are slightly above the detection limit.

The emission of unburnt pesticide is lower than 1% and lowest for the 2,4-D hydrocarbon compounds. This can be caused by the better combustion conditions in these fires. Up to now it was assumed that the emission of unburnt pesticide was 2-10%.

During the experiments it was found that the conversion of sulphur into sulphur dioxide is about 60%, and the conversion of chlorine into hydrogenchlorine equals 40 - 85%. The emissions of hydrogen sulphide, chlorine and phosgene may be neglected.

The conversion of the nitrogen in a pesticide into nitrogen oxides is very low. A maximum conversion rate of 2.4% of the nitrogen in the pesticide into nitrogen oxides has been measured during the medium scale combustion experiments. This low conversion rate probably will be caused by the poor combustion conditions. The emission of ammonia can be neglected. For dichlobenil (cyanide group containing pesticide) the emission of hydrogen cyanide is lower than 6 g/kg pesticide.

Large quantities of solid residue remain after all fires. These residues contain up to 10% of the unburnt pesticide.

Limited oxygen availability (reduced combustion air flow) did not significantly change the conversion rates into toxic products.

The idea that it is better not to extinguish a pesticide fire because the emission will increase due to the extinguishing with water is in contradiction with the results of the experiments. Water extinguishing did not significantly influence the emissions.

From the experiments it can be concluded that in general the emissions of toxic combustion products in a pesticide fire are lower than assumptions applied up to now in hazard assessments. These low emissions will be caused by the low temperatures of the fires. It should be investigated whether the conversion rates into toxic products determined during this project are also valid for fires of chemicals at higher temperatures.

Recommendations

The following emissions for a pesticide fire are suggested, taking into account the emission data of the experiments and the results of the scaling study and the uncertainties in both.

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Table 5 Suggested emissions for a pesticide fire

Component	Conversion rate		
CO	14	%	of the carbon in the pesticide
C _x H _y	3.5	%	of the carbon in the pesticide
NO _x	25	%	of the nitrogen in the pesticide
HCN	3.8	%	of the nitrogen in the pesticide
SO ₂	100	%	of the sulphur in the pesticide
HCl	100	%	of the chlorine in the pesticide
PCDD/F (TEQ)	36.10 ⁻⁷	%	of a chlorinated aromatic pesticide
Solids (soot)	16	%	of the pesticide
Pesticide	0.57	%	of the pesticide
Solid residue	32	%	of the pesticide
Residual pesticide	2.6	%	of the pesticide

Depending on the size of the fire and the availability of sufficient water catchment capacity, it may be preferable in some situations to let the fire burn instead of attempting to extinguish it. If large amounts of contaminated fire fighting water can flow into open surface water, it might be better not to use water.

Prevention and control of pesticide fires

Results

The required fire protection level for a pesticide storage depends on the product fire hazard, the packaging fire hazard, and the environmental and health hazard of the stored materials.

Criteria for the four defined fire hazard categories are the flammability of the pesticide and whether it is a gas, liquid or solid material and the flammability of the packaging material. Four fire protection levels for a pesticide storage have been defined. The fire protection levels have different requirements. For level one only basic requirements like good facility lay out, ignition source control, good housekeeping and regular training of employees are necessary. For level four automatic fire-alarms, sprinkler-systems and a basin for extinguishing water are additional requirements. The requirements of the fire protection level are given in table 3. In table 4 is indicated which fire protection level is recommended for the fire and environmental hazard category of the stored pesticides.

Recommendations

Application of the methodology is recommended to define a cost effective protection level for a pesticide storage taking into account the hazards of the stored pesticides.

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8 Project reports

- [1] Koehorst L.J.B. and M. Molag,
Toxic combustion products from pesticide fires;
Report 1: Analysis of case histories on pesticide fires,
TNO Institute of Environmental and Energy Technology, Apeldoorn
Ref. nr. 92-371, May 1989

- [2] Bartelds H.,
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Report 2: Review of small scale pesticide combustion methods,
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Ref. nr. 89-145, May 1989

- [3] Bartelds H., G. Kuipers and M. Molag,
Toxic combustion products from pesticide fires;
Report 3: Experimental results of intermediate scale Parathion,
Chlorfenvinphos, dichlobenil and 2,4-D fires,
TNO Institute of Environmental and Energy Technology, Apeldoorn
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- [4] Bartelds H.,
Toxic combustion products from pesticide fires;
Report 4: Scaling of pesticide fires,
TNO Institute of Environmental and Energy Technology, Apeldoorn
Ref. nr. 81-152, April 1991

- [5] Weger D. de, and M. Molag,
Toxic combustion products from pesticide fires;
Report 5: Prevention and control of fires in pesticide storages,
TNO Institute of Environmental and Energy Technology, Apeldoorn
Ref. nr. 81-179, May 1991

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9 Authentication

Name of the sponsors

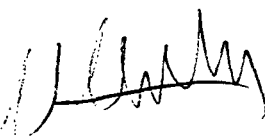
- Enichem Agricoltura, Italy;
- Joint Research Centre of the European Communities (JRC Ispra), Italy;
- Ministry for Home Affairs, Fire Services Inspectorate, The Netherlands;
- Ministry of Housing, Physical Planning and Environment, The Netherlands;
- Ministry of Social Affairs, Labour Inspectorate, The Netherlands;
- Rhône-Poulenc, France;
- Shell Internationale Chemie Maatschappij B.V., The Netherlands;
- Solvay Duphar B.V., The Netherlands;
- TNO, The Netherlands.

Names and functions of the cooperators

- H. Bartelds - projectleader combustion experiments
- M. Molag - research coordinator
- D. de Weger - scientist

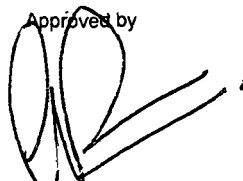
Date upon which, or period in which, the research took place
1988 - 1991

Signature



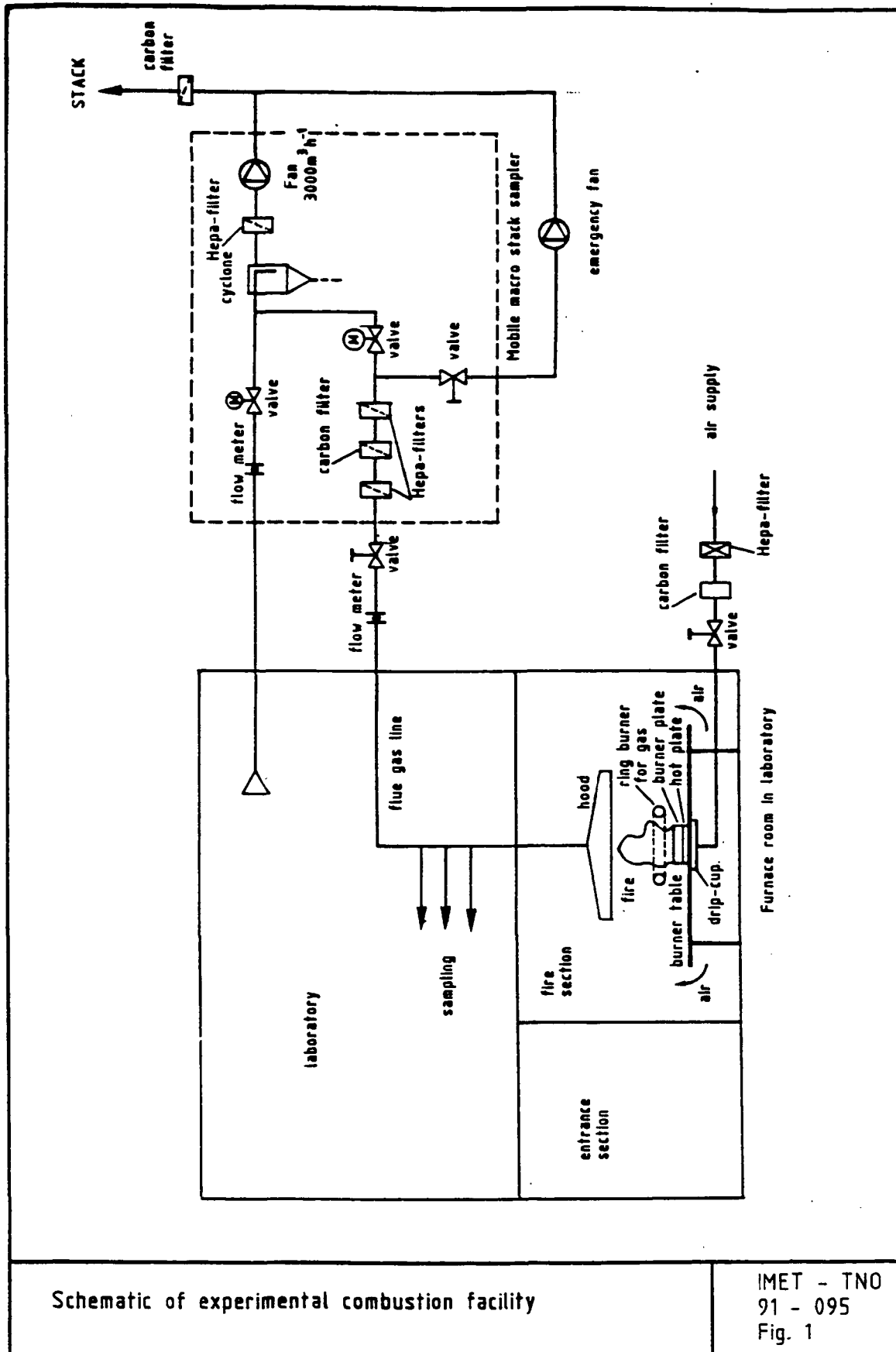
M. Molag
research coordinator

Approved by



C.M. Pietersen
section leader

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Schematic of experimental combustion facility

IMET - TNO
 91 - 095
 Fig. 1

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