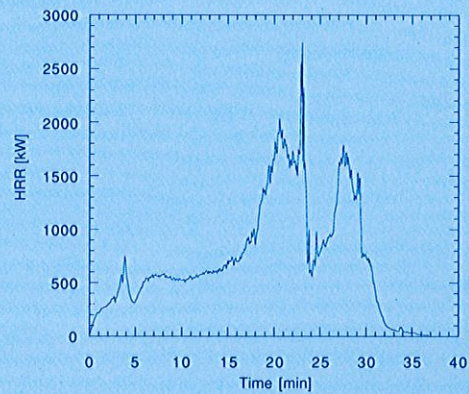
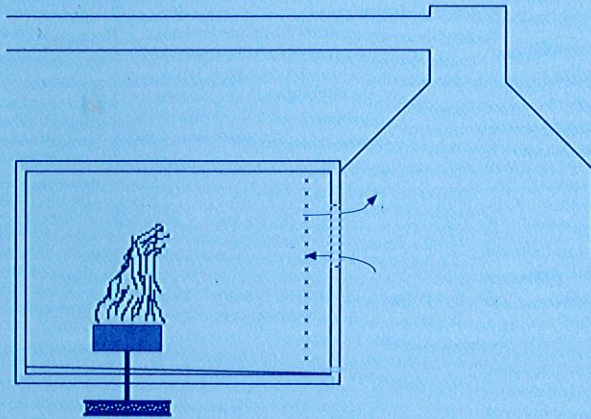


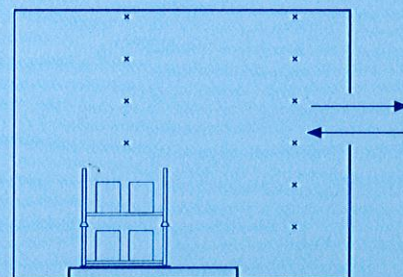
Anders Lönnermark, Vytenis Babrauskas

TOXFIRE - Fire Characteristics and Smoke Gas Analyses in Under-ventilated Large-scale Combustion Experiments

Theoretical Background and Calculations



$$\dot{m}_{out} = \frac{\frac{2}{3} \cdot C_d \cdot b \cdot h^{3/2} \cdot \sqrt{2 \cdot g \cdot (\rho_a^2 - \rho_a \cdot \rho_c)}}{\left[1 + \left[\frac{\rho_a}{\rho_c} \left(\frac{\dot{m}_{out}}{\dot{m}_{out} - \dot{m}_f} \right)^2 \right]^{1/3} \right]^{3/2}} + \dot{m}_f$$



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Abstract

Within the European research project *Guidelines for Management of Fires in Chemical Warehouses* (TOXFIRE), SP has carried out controlled large-scale combustion experiments with amount of material burned in the 100 kg range. The real challenge was to achieve conditions yielding under-ventilated, *i.e.* oxygen-depleted, combustions. Most of the large-scale experiments were carried out in the ISO 9705 room with different degrees of restrictions of the size of the door opening. Detailed analyses and characterization of the smoke gas composition were carried out during these tests. A few tests were performed in an even larger scale facility that was built to allow real storage configurations. This was done for comparison with the results from the tests in the ISO 9705 room and the analysis were not as detailed.

This report describes the evaluation techniques and calculation procedures used to characterize the fire dynamics such as heat release rate, mass loss rate, mass flow of air and fire gases in the opening of the test compartment, equivalence ratio and combustion efficiency.

Much effort was put into developing a "generalized carbon dioxide generation" scheme for computing the heat release rate. For under-ventilated experiments, when the combustion is far from complete, it is not enough only to study the carbon dioxide generation. Therefore, also the generation of carbon monoxide, soot and unburned hydrocarbons have been included. The generalized CO₂ scheme is valuable for use in cases where satisfactory oxygen consumption data cannot be experimentally obtained. Validation tests showed that this method is as good as oxygen consumption calorimetry (OCC) when the correct factor for the energy per kg oxygen consumed (E) was used and it should be better than the general OCC where a constant value, E = 13.1 MJ released energy per kg oxygen consumed, often is used irrespective of material.

To experimentally determine the equivalence ratio during a test, a *phi meter* was constructed. The instrumental set-up is described and the relation to the equivalence ratio explained.

Since a majority of the measurements were performed in the compartment opening, it was necessary to know the instant mass flow of gases in the opening. The calculations of the mass flow were based on temperature measurements and the mass loss rate of the fuel. The derivation of a mathematical formula is described in the report.

Key words: Heat release rate, carbon dioxide, mass flow, equivalence ratio

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Table of contents

	Abstract	2
	Table of contents	3
	Foreword	4
	Nomenclature	5
1	Introduction	9
2	Experiments	11
3	Mass loss rate	14
4	Mass flow out of the room	16
5	Equivalence ratio	20
5.1	Definition of the equivalence ratio	20
5.2	The phi meter	21
6	Opening sizes	30
7	Chemical reactions	32
8	Compensation for the water removal in the carbon monoxide and carbon dioxide measurements	35
9	Heat release rate	38
9.1	Heats of combustion and heats of formation	39
9.2	Heat release rate formulas	42
10	Combustion efficiency	46
11	Validation tests	48
12	Evaluation of chloronitrobenzoic acid	49
13	Conclusions	51
14	References	52

Foreword

This study is part of the CEC-project *Guidelines for Management of Fires in Chemical Warehouses* (TOXFIRE) within the CEC ENVIRONMENT programme (contract no. EV5V-CT93-0275). The work has been sponsored by The Swedish National Board for Industrial and Technical Development, and The Swedish Rescue Services Agency.

We would like to thank our colleagues at the department of Fire Technology for valuable assistance throughout this work. We would also like to thank Margret Månsson at the department of Chemical Analysis for advice and, in particular, for her help regarding calorimetric values for different chemical compounds.

Nomenclature

A	Area [m^2]
A	Constant in the curve fit of p_a (= 23.2)
a	The ratio between the number of moles of H_2O and CO_2 produced in a complete combustion according to the stoichiometric coefficients
B	Constant in the curve fit of p_a (= 3816)
b	Width of the opening of the combustion compartment [m]
C	Constant in the curve fit of p_a (= 46)
C_d	Discharge coefficient (0.68 used in calculations)
E	Heat released per unit mass of O_2 consumed [$\text{MJ}/\text{kg}_{\text{O}_2}$]
g	Acceleration of gravity [m/s^2]
h	Height of the opening of the combustion compartment [m]
ΔH_c	Heat of combustion when gaseous products (net heat of combustion) [kJ/mol]
Δh_c	Heat of combustion when gaseous products (net heat of combustion) [MJ/kg]
ΔH_f	Heat of formation [kJ/mol]
ΔH_r	Heat of reaction [kJ/mol]
Δh_r	Heat of reaction [MJ/kg]
I	Intensity for a parallel light beam measured in the lamp-photo cell system in the duct with a smoky environment [W/m^2]
I_0	Intensity for a parallel light beam measured in the lamp-photo cell system in the duct with a smoke free environment [W/m^2]
k	Extinction coefficient [m^{-1}]
L	Length (of the diameter of the duct) [m]
M	Molecular weight [g/mol]
m	Mass [kg]
\dot{m}	Mass loss rate [kg/s]
\dot{m}	Mass flow rate [kg/s]
n	Number of moles
p	Pressure [Pa]
Q	Energy [MJ]
\dot{Q}	Heat release rate [MW]
$\dot{Q}_{\rightarrow \text{product}}$	Heat release rate when a certain <i>product</i> is produced [MW]
R	Ideal gas constant [$\text{J}/(\text{K} \cdot \text{mol})$]
RH	Relative humidity [%]
R_{inst}	Instantaneous rate of light-obscuring smoke [m^2/s]
r	Stoichiometric air/fuel mass ratio
t	Time [min]
T	Temperature [K]
V	Volume [m^3]
\dot{V}	Volume flow rate [m^3/s]
v	Velocity in the opening (normally to the opening surface) of the combustion compartment [m/s]
X	Number of moles produced of a molecule per mole substance consumed
x	Mole fraction
	Volume fraction
Y	Mass fraction [kg/kg]

y Height above the neutral plane in the combustion compartment [m]

Greek symbols

χ Combustion efficiency
 ϕ Equivalence ratio
 ρ Density [kg/m³]
 ρ_c Density inside the combustion compartment [kg/m³]

Subscripts

a Ambient air
c Compartment
Combustion
d Duct
f Fuel
Formation
in Corresponds to the inflow through the opening
out Corresponds to the outflow through the opening
product Relates to a certain *product* in a chemical reaction (*e.g.* CO₂)
r Reaction
s Saturation conditions
T Calculated from temperature measurements
tot Total
w Water application
 ϕ Calculated from phi meter measurements

Superscripts

+ Corresponds to the extra flow of oxygen added in the phi meter
a Ambient air
c Combustion
dry Gas analysed after that water has been trapped out
i Corresponds to the conditions at the oxygen analyser in the phi meter when extra oxygen is added but only ambient air is present at the inlet
st Stoichiometric
w Water application
wet Corresponds to the conditions for a gas before water has been trapped out

Operator

Time derivative

Abbreviations

calc. Calculated
CB Monochlorobenzene
CGC Carbon dioxide generation calorimetry
CNBA 4-chloro-3-nitrobenzoic acid
f.b. Free burning

FC	Furniture calorimeter
FID	Flame ionisation detector
g	Gas
GER	Global equivalence ratio
GSP	Gas sampling probe
HRR	Heat release rate
IC	Industry calorimeter
l	Liquid
MLR	Mass loss rate
Ny	Nylon 66
OCC	Oxygen consumption calorimetry
PMMA	Polymethylmetaacrylate
PMP	Phi meter probe
PP	Polypropene
ref.	Reference
s	Solid
s.c.	Storage configuration
SCTE	Storage configuration test enclosure
SPR	Smoke production rate
SSP	Soot sampling probe
stoich.	Stoichiometric
THC	Total amount of unburned hydrocarbon
TMTM	Tetramethylthiuram monosulfide
t.t.c.	Two-tier configuration

1 Introduction

In many countries there are large numbers 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 chemical storage facilities.

The project *Guidelines for Management of Fires in Chemical Warehouses* (TOX-FIRE) 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 (coordinator)
- NERI - Danish National Environmental Research Institute
- South Bank University, United Kingdom
- VTT - Technical Research Centre of Finland
- Lund University, Sweden
- SP - Swedish National Testing and Research Institute
- FOA - Swedish National Defence Research Establishment

Based on a number of characteristics, the substances were classified comprising ignitability, heat release, burning rate, smoke production, combustion products and the influence of the packaging materials on the combustion products. The source characteristics were described by parameters obtained by carrying out combustion experiments at various scale and by studying the effects of scaling. In addition, the fire scenarios were characterized by the degree of ventilation, the packaging materials, the stacking of the materials and the response of the building. Also the suppression was an important parameter, *i.e.* active and passive suppression and the fire brigade tactics.

The consequences to humans as well as the environment were assessed in the project. The existing modelling methods used for risk assessment were studied, along with the handling and prevention of the accidents. These investigations led 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, a quick decision system to be used by the fire chief in the case of chemical fire was also developed.

The role of SP in the TOXFIRE project was to determine the source characteristics by carrying out controlled large-scale combustions with amount of material burned in the 100 kg range. The aim was to provide results as close to real scale as possible for comparison with results from the smaller scale measurements in the project. The real challenge was to achieve conditions yielding under-ventilated, *i.e.* oxygen-depleted, combustions. Most of the large-scale experiments were carried out in the ISO 9705 room with different degrees of restrictions of the size of the door opening. A few tests were performed in a larger scale test facility that was built to allow real storage configurations. The SP work was carried out in co-operation between the departments of Fire Technology and Chemical Analysis.

A phi meter was used to define the degree of ventilation. In addition to the common fire test parameters mentioned previously, extensive measurements were carried out to characterize the composition of the smoke gases. On-line measurements, *e.g.* Fourier Transform InfraRed spectroscopy (FTIR), and adsorbent techniques were utilized to measure quantitatively individual components in the smoke. Measurements of the mass loss rate allowed evaluation of yields in relation to amount of material burned for the various species in the smoke gases.

This report describes a method for using a "generalised carbon dioxide generation" scheme for computing the heat release rate. It also contains descriptions of the evaluation techniques and calculation procedures used for characterizing other fire related parameters such as mass loss rate, mass flow of air and fire gases in the opening of the test compartment, equivalence ratio and combustion efficiency.

This is the first time that detailed steps have been published showing how to set up the equations so that the generation rates of CO₂ and other combustion products could be used to estimate the HRR. This technique is much more difficult to apply than the conventional oxygen consumption calorimetry, where only a single material constant is needed, and even that constant is typically a universal constant. The generalised CO₂ scheme, however, is valuable for use in cases where satisfactory oxygen consumption data could not be obtained experimentally.

The remainder of the SP work in the TOXFIRE project is accounted for in a set of five additional reports [1 - 5].

2 Experiments

This report mainly describes the theories and evaluation procedures used within the TOXFIRE project and is not a presentation of the experimental details. Such information can instead be found in the references 2 and 3. There is also a description of the tested substances available. A short description of the test set-ups is however included below to give some understanding of the experimental situation. Figure 2.1 shows the experimental set-up used in the main test series and some experimental conditions are given in Table 2.1.

The aim was to study the combustion chemistry when chemicals are burning in different ventilation conditions. Especially under-ventilated conditions were of interest. To obtain this, different opening heights (0.45 m, 0.56 m, 0.68 m and 0.89 m) were used (see Table 2.1 and Chapter 6). The width of the opening was 0.8 m in all the tests.

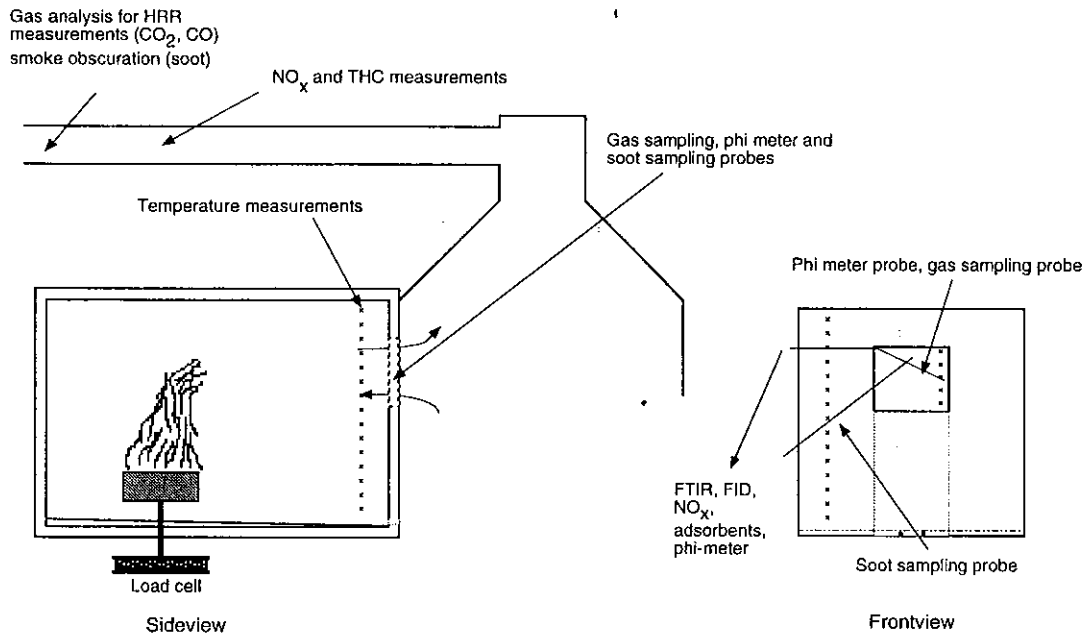


Figure 2.1 The large scale experiment set-up including the ISO 9705 room [6] with the dimensions $3.6 \text{ m} \times 2.4 \text{ m} \times 2.4 \text{ m}$ and the measurement stations in the opening and in the exhaust duct to the calorimeter system.

To allow a real storage configuration, a storage configuration test enclosure (SCTE) [3] was built (see Figure 2.2) beneath the industry calorimeter [7,8] in SP's fire hall. In most of the storage configuration tests, the substances were packed in small paper bags which were then put into cardboard boxes ($0.4 \text{ m} \times 0.6 \text{ m} \times 0.5 \text{ m}$). Eight boxes were placed in a two-tier configuration (t.t.c.) with four boxes on each level. In a few tests a fuel pan/load cell set-up, like the one in the large scale tests, was used.

Table 2.1 *Experimental conditions for the large scale tests given in order of performance [2]. The abbreviations in the identification of the tests are explained in Nomenclature at the beginning of the report.*

Test	Fuel mass /kg	Pool size /m ²	Opening height, <i>h</i> /m
PP3	60	1.2	0.89
PP4	60	1.2	0.56
PP5	60	1.2	0.68 1)
PP6	60	1.2	0.45
Ny2	75	1.4	0.89
Ny3	55	1.4	0.56
Ny4	75	1.4	0.68 1)
Ny5	75	1.4	0.45
TMTM2	60	1.2	0.89
TMTM3	60.5	1.2	0.56
TMTM4	60	1.2	0.68 1)
TMTM5	60.5	1.2	0.45
CNBA1	74.5	1.4	0.89 3)
CNBA2	60 + 10 2)	1.4	0.89 3)
CNBA3	40 + 5 2)	1.4	0.89 3)
CB3	45	0.5	0.89 3)
CB4	51	0.8	0.89 3)
CB5	50.5	0.8	0.45 3)
CNBA4	60 + 10 2)	1.4	0.89
CB6	50	0.8	0.68 1)

1) A water applicator was used during portions of this test.

2) Mass CNBA + mass PP [kg]

3) Dioxin formation was measured during this test [9].

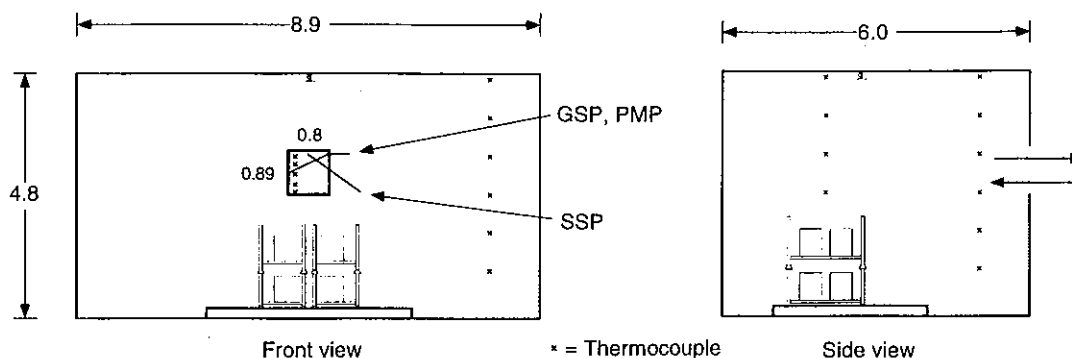


Figure 2.2 The storage configuration test enclosure. The substance were put into eight cardboard boxes, which were placed in a two-tier configuration. Three different probes were used for the sampling: the gas sampling probe (GSP), the phi meter probe (PMP) and the soot sampling probe (SSP). This is described in the references 2 and 3. Dimensions in m.

The ISO room was thought to be large enough to give results representative for a real chemical storage situation (not the amount of fuel, but in the way the substance reacted in an under-ventilated fire). The tests in the SCTE were performed to confirm this idea and also to study the effects of storage configuration on the results. For this reason and due to the large amount of fuel needed in the storage configuration tests, only six tests were performed inside the SCTE (see Table 2.2). In the number describing the mass of the fuel, only the mass of the studied substance, and not the mass of the cardboard, is included. Two of the storage configuration tests were free burning (f.b.) under the industry calorimeter.

Table 2.2 Experimental conditions for the storage configuration tests given in chronological test order. t.t.c. refers to the two-tier configuration described above [3].

Test*	Fuel mass /kg	Pool size /m ²	Opening height, <i>h</i> /m
PP7	130	t.t.c.	f.b.
CB2	20	**	f.b.
PP8	42.5	1.2	0.89
PP9	160	t.t.c.	0.89
Ny6	160	t.t.c.	0.89
TMTM6	160	t.t.c.	0.89
CNBA5	160	t.t.c.	0.89
CB7	39.5	0.8	0.89

* The abbreviations in the identification of the tests are explained in Nomenclature at the beginning of the report.

** Polyethene bottles with chlorobenzene were placed in one cardboard carton.

3 Mass loss rate

The mass and the mass loss were measured with a load cell. From this data, mass loss rate (MLR) can be obtained by differentiation. Due to turbulence inside the room and other disturbances during the combustion tests, the differentiated signal could be very noisy. Therefore different courses of action were taken depending on the magnitude of the disturbances. This was not an overall decision, but decisions were made after separate considerations for each case. The tools used were different functions within the software KaleidaGraph™ [10]. The functions are called "Polynomial" (fits a curve with an Nth order polynomial curve, $N \leq 9$), "Smooth" (computes a M-points moving average surrounding the current data point) and "Weighted" (fits a curve to the data, using what is called the locally weighted least squared error method; a smoothing factor can here be modified to control the fraction of the data population that should be considered during the smoothing process).

In the computation of a useful MLR curve these functions were used on the original mass data, on the calculated MLR data points or both. The operators used in the process are described by the label of the MLR curve (see Figure 3.1). For example, "MLRwgh0%" means that MLR was calculated from the original data and then a weighted function without any smoothing was applied to the MLR data; "MLR(Mpol9)" means that MLR was calculated from a 9th order polynomial fit of the original load cell signal. In two of the tests in the SCTE [3], a pan/load cell set-up was used. In those cases the signal from the load cell was disturbed by the heat inside the enclosure. The pool fires where, however, burning very slowly and it was therefore assumed that the MLR curve and the HRR curve had the same shape. This meant that the MLR could be calculated from the HRR since the total mass loss was known.

In Table 3.1 below, the different operators used for each test are presented. A couple of tests are presented as examples in Figure 3.1. The curves labelled only "MLR" are calculated directly from the load cell signal without any curve fits; these curves are included for comparison.

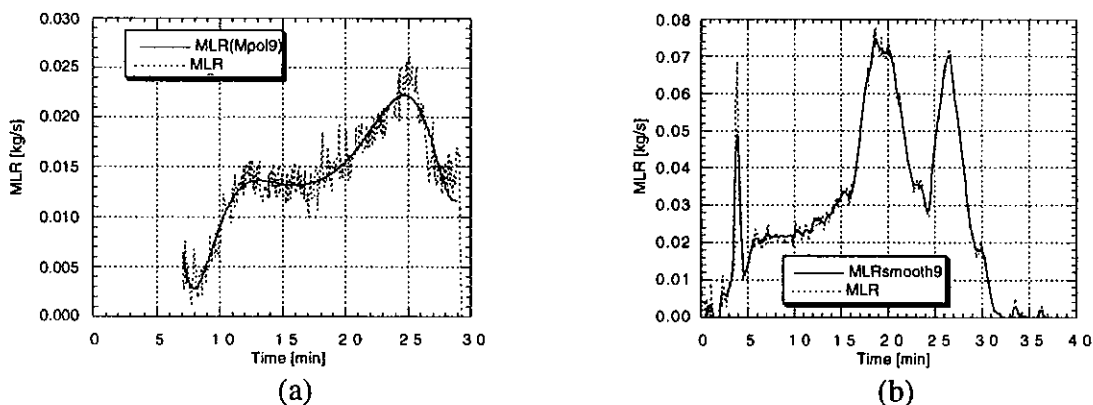


Figure 3.1 Example of "original" and fitted MLR curves: a) Ny5 and b) TMTM4.

Table 3.1 The curve fits used on the mass or the MLR data for the different tests. The capital M inside the parentheses indicates that the curve fit was performed on the mass signal before the MLR was calculated.

Test	MLR calculations	Test	MLR calculations
PP3	MLRwgh0%	CNBA1	MLR(Mpol9)
PP4	MLR(Mpol9)	CNBA2	MLRsmooth9
PP5	MLR(Mpol9)	CNBA3	MLRsmooth9
PP6	MLR(Mwgh20%)	CNBA4	MLR
Ny2	MLR(Mpol9)	CB3	MLRsmooth9
Ny3	MLR(Mpol9)	CB4	MLR(Mpol9)
Ny4	MLR(Mpol9)	CB5	MLR(Mwgh5%)
Ny5	MLR(Mpol9)	CB6	MLR(Mpol9)
TMTM2	MLR(Mpol9)	PP8	MLR(HRR)
TMTM3	MLRsmooth9	CB7	MLR(HRR)
TMTM4	MLRsmooth9		
TMTM5	MLR(Mpol9)		

4 Mass flow out of the room

It is a very difficult task to use velocity and temperature sensors in the opening plane in order to establish the mass flow rates. With a high degree of attention to detail, such techniques can be used for steady state fires [11, 12]. However, for transient fires, when similar techniques are applied, the results are often nonsensical [13]. This depends on the following three different facts.

- (1) The outflows in the doorway opening have a velocity component in directions other than just the normal to the exit plane. With the commonly available velocity probes, this component is partially assigned – erroneously – to the normal direction.
- (2) For some fires the velocity distribution is not uniform across the width of the opening. Not only is the velocity different near the edges of the opening, but some fires show [13] a stagnant region near the centre and higher velocity flows away from the centre.
- (3) The velocity measurements obtained are usually highly noisy, since the pressure difference is only a few pascals due to the low flow.

The above considerations suggest that the mass flows in the opening should be computed by some means, rather than using direct measurement techniques. For post-flashover fire conditions it can be shown (and it will be discussed further down in the text) that the mass flow into the room through the opening can be approximated by

$$\dot{m}_{in} \approx 0.5 \cdot A \cdot \sqrt{h} \text{ kg/s} \quad (4.1)$$

where A is the area of the opening [m^2] and h is the height of the opening [m]. This formula was used to estimate the opening size required to obtain a certain degree of under-ventilation (see Chapter 6). For some of our analysis purposes, it was however not enough to use this simplest approximation for mass flow in-and-out of the room. A more precise value of the mass flow out of the room was desirable, since many measurements were performed in the opening and the accuracy of the calculated results (*e.g.* yields) from those measurements very much depended on the accuracy of the computed value of the outflow.

The model chosen was described by Babrauskas [14]. The model assumes a well-stirred uniform-temperature compartment which means that the density inside the compartment should be uniform. Babrauskas compares the pressures inside and outside the room, respectively, uses Bernoulli's equation and ends up with the following equations for the velocities:

$$v_{out} = \sqrt{2 \cdot g \cdot y \cdot \left(\frac{\rho_a}{\rho_c} - 1 \right)} \quad (4.2)$$

and

$$v_{in} = \sqrt{2 \cdot g \cdot y \cdot \left(\frac{\rho_c}{\rho_a} - 1 \right)} \quad (4.3)$$

where

g = acceleration of gravity [m/s²]

ρ_a = density of ambient air [kg/m³]

ρ_c = density inside the compartment [kg/m³]

y = height above the neutral plane [m]

If the heights of the outflowing and the inflowing layers are denoted h_{out} and h_{in} (defined to always represent positive numbers), respectively, the mass flows can be calculated from the following formulas

$$\dot{m}_{out} = C_d \cdot b \cdot \rho_c \cdot \int_0^{h_{out}} v_{out} \cdot dy \quad (4.4)$$

$$\dot{m}_{in} = C_d \cdot b \cdot \rho_a \cdot \int_{-h_{in}}^0 v_{in} \cdot dy \quad (4.5)$$

where

C_d = discharge coefficient

b = opening width [m]

Performing the integrations gives

$$\dot{m}_{out} = \frac{3}{2} \cdot C_d \cdot b \cdot (h_{out})^{3/2} \cdot \rho_c \cdot \sqrt{2 \cdot g \cdot \left(\frac{\rho_a}{\rho_c} - 1 \right)} \quad (4.6)$$

$$\dot{m}_{in} = \frac{3}{2} \cdot C_d \cdot b \cdot (h_{in})^{3/2} \cdot \rho_a \cdot \sqrt{2 \cdot g \cdot \left(1 - \frac{\rho_c}{\rho_a} \right)} \quad (4.7)$$

Using the approximation that $\dot{m}_{in} = \dot{m}_{out}$ and the relation $h_{in} + h_{out} = h$ gives

$$h_{out} = h \cdot \frac{1}{1 + \left(\frac{\rho_c}{\rho_a}\right)^{1/3}} \quad (4.8)$$

$$h_{in} = h \cdot \frac{1}{1 + \left(\frac{\rho_a}{\rho_c}\right)^{1/3}} \quad (4.9)$$

and

$$\dot{m}_{out} = \frac{2}{3} \cdot C_d \cdot b \cdot h^{3/2} \cdot \rho_c \cdot \sqrt{2 \cdot g} \cdot \sqrt{\frac{\rho_a - 1}{\rho_c}} \cdot \sqrt{\frac{1}{\left(1 + \left(\frac{\rho_c}{\rho_a}\right)^{1/3}\right)^3}} \quad (4.10)$$

$$\dot{m}_{in} = \frac{2}{3} \cdot C_d \cdot b \cdot h^{3/2} \cdot \rho_a \cdot \sqrt{2 \cdot g} \cdot \sqrt{\frac{1 - \rho_c}{\rho_a}} \cdot \sqrt{\frac{1}{\left(1 + \left(\frac{\rho_a}{\rho_c}\right)^{1/3}\right)^3}} \quad (4.11)$$

Babrauskas showed that the last square-root-factor can be approximated as 0.21 (for post-flashover fires) [14]. With ρ_a as 1.21 kg/m³ (at 293 °K), g as 9.817 m/s² and C_d as 0.68 the flow can be approximated with

$$\dot{m}_{in} \approx 0.51 \cdot A \cdot \sqrt{h} \text{ kg/s}$$

which is the formula mentioned earlier.

The mass flow formulas above are valid under the approximation that $\dot{m}_{in} = \dot{m}_{out}$, but if one wants to consider also the mass loss rate, \dot{m}_f , one gets

$$h_{out} = h \cdot \frac{\frac{\rho_a^{1/3}}{\rho_c^{1/3}} \cdot \left(\frac{\dot{m}_{out}}{\dot{m}_{out} - \dot{m}_f}\right)^{2/3}}{1 + \frac{\rho_a^{1/3}}{\rho_c^{1/3}} \cdot \left(\frac{\dot{m}_{out}}{\dot{m}_{out} - \dot{m}_f}\right)^{2/3}} \quad (4.12)$$

Using this relation in Equation (4.6) finally gives

$$\dot{m}_{out} = \frac{\frac{2}{3} \cdot C_d \cdot b \cdot h^{\frac{3}{2}} \cdot \sqrt{2 \cdot g \cdot (\rho_a^2 - \rho_a \cdot \rho_c)}}{\left[1 + \left[\frac{\rho_a}{\rho_c} \left(\frac{\dot{m}_{out}}{\dot{m}_{out} - \dot{m}_f} \right)^2 \right]^{\frac{1}{3}} \right]^{\frac{3}{2}}} + \dot{m}_f \quad (4.13)$$

which has to be solved numerically by *e.g.* iteration. This formula was used to calculate the mass flow rate during the tests in the series of experiments (see Chapter 2).

5 Equivalence ratio

5.1 Definition of the equivalence ratio

A parameter increasingly used to describe the ventilation conditions during fires is the equivalence ratio, ϕ , defined as

$$\phi = \frac{\dot{m}_{fuel}/\dot{m}_{oxygen}}{\left(\dot{m}_{fuel}/\dot{m}_{oxygen}\right)_{stoich.}} \quad (5.1)$$

$\phi = 1$ stoichiometric combustion
 $\phi < 1$ well-ventilated combustion
 $\phi > 1$ under-ventilated combustion

i.e. the actual fuel/oxygen ratio is compared with the stoichiometric fuel/oxygen ratio. For the calculation of ϕ , molar ratios instead of mass ratios may be used in the formula. Since it is the over-all combustion process and not the spatial variations that is studied in this work, ϕ is defined in a wider sense as the equivalence ratio for the total combustion process. This is usually called the global equivalence ratio, GER. In this case the definition of the GER is the ratio between the MLR of the fuel and the mass flow of oxygen entering the combustion room normalized by the stoichiometric ratio.

In the mass flow calculations described above, the total flow is considered and not just the flow of oxygen. Therefore it is more convenient to be able to use the air flow instead of the oxygen flow in the formulas. This can also be done which is demonstrated in the following formula transformation.

$$\dot{m}_{N_2} = \frac{x_{N_2} \cdot M_{N_2}}{x_{O_2} \cdot M_{O_2}} \cdot \dot{m}_{O_2} \quad (5.2)$$

where the values of the molecular weights in Table 9.3 were used.

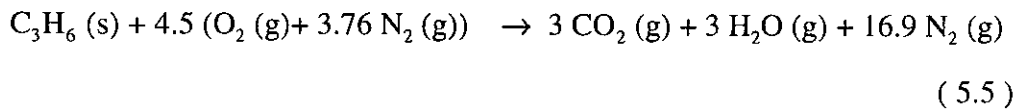
$$\frac{\dot{m}_f}{\dot{m}_{air}} = \frac{\dot{m}_f}{\dot{m}_{O_2} \cdot \left(1 + \frac{x_{N_2} \cdot M_{N_2}}{x_{O_2} \cdot M_{O_2}}\right)} = \frac{\dot{m}_f}{\dot{m}_{O_2}} \cdot \frac{1}{\left(1 + \frac{x_{N_2} \cdot M_{N_2}}{x_{O_2} \cdot M_{O_2}}\right)} \quad (5.3)$$

$$\left(\frac{\dot{m}_f}{\dot{m}_{air}}\right)_{stoich.} = \frac{\dot{m}_f}{\dot{m}_{O_2} \cdot \left(1 + \frac{x_{N_2} \cdot M_{N_2}}{x_{O_2} \cdot M_{O_2}}\right)_{stoich.}} \cdot \frac{1}{\left(1 + \frac{x_{N_2} \cdot M_{N_2}}{x_{O_2} \cdot M_{O_2}}\right)_{stoich.}}$$

Consequently, the fuel/air mass ratio can be used instead of the fuel/oxygen mass ratio and ϕ can be calculated as

$$\phi = \frac{\dot{m}_f}{\dot{m}_{air}} \equiv \frac{\dot{m}_f}{\left(\frac{\dot{m}_f}{\dot{m}_{air}}\right)_{stoich.}} = \frac{\dot{m}_f}{\frac{1}{r} \dot{m}_{air}} = \frac{\dot{m}_f \cdot r}{\dot{m}_{air}} \quad (5.4)$$

where r is defined as the stoichiometric air/fuel mass ratio. To be able to calculate ϕ , this constant must be determined for the different substances and to do so also the air nitrogen needs to be included in the chemical formulas given in Chapter 7. In air the molar ratio of nitrogen to oxygen is approximately $79/21 \approx 3.76$. For instance, the combustion of polypropene in air is represented as:



which means that 1 mole $\text{C}_3\text{H}_6 \leftrightarrow 4.5$ moles $(\text{O}_2 + 3.76\text{N}_2)$. Since the mole masses of polypropene and the group inside the parentheses are 42.04 g/mol and 137.3 g/mol, respectively, this is the same relation as 1 kg $\text{C}_3\text{H}_6 \leftrightarrow 14.70$ kg air. If the corresponding calculations are performed for the other substances one gets the values presented in Table 5.1

Table 5.1 The stoichiometric air/fuel mass ratios for different substances.

Substance	r (m_{air}/m_{fuel}) / (kg/kg)
Polypropene	14.70
Nylon	10.02
TMTM	7.91
CNBA	3.92
Chlorobenzene	8.54

5.2 The phi meter

To determine, experimentally, the ventilation conditions inside the room, a new apparatus, the *phi meter* [15], was used. The essential parts of the phi meter are the combustor, into which the fire gases and additional pure oxygen are introduced, and the O_2 analyser (see Figure 5.1). In the combustor, heated by a tube furnace, complete combustion of the fire gases is achieved, using the added oxygen and helped by a catalyst. The readings on the O_2 analyser (*M&C Instruments b.v. Oxygen Analyser Type PMA 10*) are compared with background measurements without fire gases at the inlet. A simple computation gives the equivalence ratio. The way to the final equation, however, needs some explanation.

First it should be mentioned that the whole theory is based on the assumption that only oxygen and nitrogen reach the oxygen analyser. That is why all the dryers and traps are needed. The theory is developed for fuels containing only carbon, hydrogen and oxygen, *i.e.* fuels that would give only CO_2 and H_2O as products after a complete combustion. Therefore only CO_2 and H_2O traps are included. The possible problem with other products in the combustion gases will be discussed later.

After the combustor, the combustion gases flowed through a short pipe of stainless steel and through a in-line soot filter. The gases were cooled by a Peltier cooler (*Supercool DA-101-24-02*). The line of traps consisted of a H_2O trap with Drierite (active ingredient CaSO_4), a glass tube with Ascarite (active ingredient NaOH) to trap CO_2 and magnesium perchlorate to trap H_2O , and one more trap with Drierite. This last trap was added to ensure that no water reached the mass flow controller. The colour change of Drierite when used also indicated if the H_2O trap with magnesium perchlorate was working as it should. When the NaOH reacted with CO_2 , much heat and water were produced. To avoid clogging of the CO_2 trap, sand was mixed with the Ascarite.

The flow of oxygen was 0.25 L/min and the flow through the oxygen analyser was 0.5 L/min. These flows were controlled by a stainless steel mass flow control system (*Aalborg AFC 2600*).

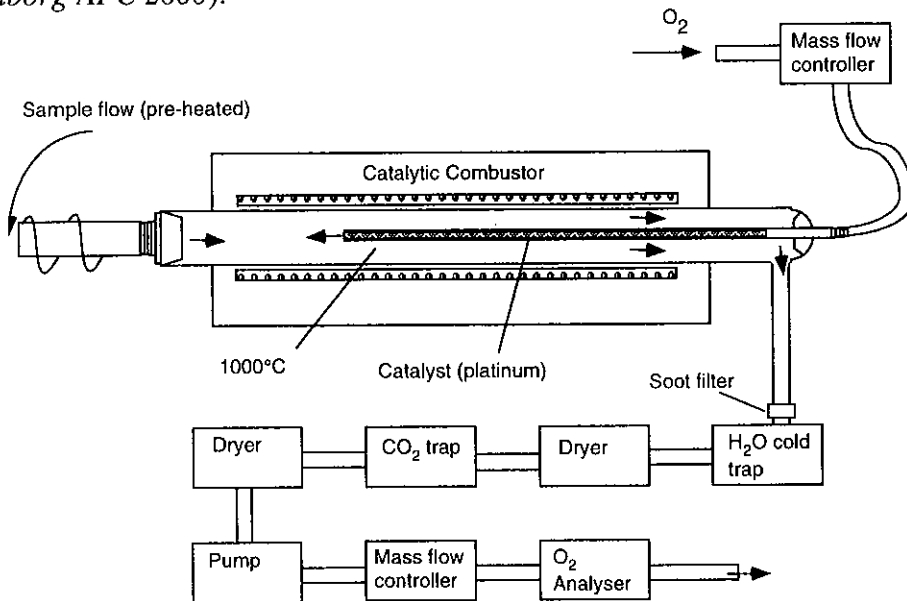


Figure 5.1 The phi meter, an instrument for measuring the equivalence ratio

Following the strategy described by Babrauskas et al. [15], the derivation of the final equation will be divided into two steps, one concerning only well-ventilated fires where extra oxygen is not needed and one where also under-ventilated fires will be considered.

Step 1 ($\phi < 1$) no additional oxygen required

With the following definitions

\dot{n}_f = the molar flow of fuel entering the combustion zone

$\dot{n}_{O_2}^a$ = the molar flow of ambient oxygen

\dot{n}_{O_2} = the molar flow of oxygen at the oxygen analyser

$\dot{n}_{O_2}^{st} = \dot{n}_{O_2}^a - \dot{n}_{O_2}$ = the molar flow of oxygen needed for complete combustion of the entering sample gas

the equivalence ratio can be expressed as

$$\phi_1 = \frac{\dot{n}_f / \dot{n}_{O_2}^a}{\dot{n}_f / \dot{n}_{O_2}^{st}} = \frac{\dot{n}_{O_2}^{st}}{\dot{n}_{O_2}^a} = \frac{\dot{n}_{O_2}^a - \dot{n}_{O_2}}{\dot{n}_{O_2}^a} \quad (5.6)$$

Dividing both the numerator and the denominator by $\dot{n}_{N_2}^a$, assuming that the nitrogen does not take part in the combustion process so that

$$\dot{n}_{N_2} = \dot{n}_{N_2}^a \quad (5.7)$$

yields

$$\phi_1 = \frac{\dot{n}_{O_2}^a / \dot{n}_{N_2}^a - \dot{n}_{O_2} / \dot{n}_{N_2}}{\dot{n}_{O_2}^a / \dot{n}_{N_2}^a} \quad (5.8)$$

but

$$\frac{\dot{n}_{O_2}^a}{\dot{n}_{N_2}^a} = \frac{x_{O_2}^a}{x_{N_2}^a} \quad \text{and} \quad \frac{\dot{n}_{O_2}}{\dot{n}_{N_2}} = \frac{x_{O_2}}{x_{N_2}} \quad (5.9)$$

and

$$\dot{n}_{tot}^a = \dot{n}_{O_2}^a + \dot{n}_{N_2}^a \quad \text{and} \quad \dot{n}_{tot} = \dot{n}_{O_2} + \dot{n}_{N_2} \quad (5.10)$$

where

$x_{O_2}^a$ and $x_{N_2}^a$ = the ambient mole fractions of oxygen and nitrogen, respectively

x_{O_2} and x_{N_2} = the mole fractions of oxygen and nitrogen at the analyser

Since all other molecules but for oxygen and nitrogen are removed, the sum of the oxygen mole fraction and the nitrogen mole fraction equals one. Therefore

$$\begin{aligned}\phi_1 &= \frac{x_{O_2}^a/x_{N_2}^a - x_{O_2}/x_{N_2}}{x_{O_2}^a/x_{N_2}^a} = \frac{x_{O_2}^a/(1-x_{O_2}^a) - x_{O_2}/(1-x_{O_2})}{x_{O_2}^a/(1-x_{O_2}^a)} \\ &= 1 - \frac{x_{O_2}}{x_{O_2}^a} \cdot \frac{(1-x_{O_2}^a)}{(1-x_{O_2})}\end{aligned}\quad (5.11)$$

Step 2 (all values of ϕ) additional oxygen is required

Here the molar flow of the extra oxygen, $\dot{n}_{O_2}^+$, is added to the list of molar flows so that

$$\dot{n}_{O_2}^{st} = \dot{n}_{O_2}^+ + \dot{n}_{O_2}^a - \dot{n}_{O_2} \quad (5.12)$$

which means that the equivalence ratio can be written in a similar way as done above

$$\phi = \frac{\dot{n}_{O_2}^+/\dot{n}_{N_2} + \dot{n}_{O_2}^a/\dot{n}_{N_2}^a - \dot{n}_{O_2}/\dot{n}_{N_2}}{\dot{n}_{O_2}^a/\dot{n}_{N_2}^a} = \phi_2 + \phi_1 \quad (5.13)$$

where ϕ_1 is the same as in step 1. To develop ϕ_2 further, the ideal gas law will be used together with the relation

$$\dot{V}_{N_2} = \dot{V} \cdot (1 - x_{O_2}) \quad (5.14)$$

i.e.

$$\dot{n}_{O_2}^+ = \frac{\dot{V}_{O_2}^+ \cdot p^+}{R \cdot T^+} \quad (5.15)$$

$$\dot{n}_{N_2} = \frac{\dot{V}_{N_2} \cdot p}{R \cdot T} = \frac{\dot{V} \cdot p \cdot (1 - x_{O_2})}{R \cdot T} \quad (5.16)$$

$$\phi_2 = \frac{\dot{n}_{O_2}^+/\dot{n}_{N_2}}{\dot{n}_{O_2}^a/\dot{n}_{N_2}^a} = \frac{(1 - x_{O_2}^a) \cdot \dot{V}_{O_2}^+ \cdot p^+ \cdot T}{x_{O_2}^a \cdot (1 - x_{O_2}) \cdot \dot{V} \cdot p \cdot T^+} \quad (5.17)$$

where \dot{V} is the total volume flow out at the oxygen analyser (must be constant during the test for the rest of the theory to apply) and $\dot{V}_{O_2}^+$ is the oxygen volume flow in the added stream. If one assumes that $T = T^*$ and $p = p^*$, these parameters can be omitted. With the definitions above of the volume flow one can write the volume inflow of oxygen as

$$\dot{V}_{O_2}^a = (\dot{V} - \dot{V}_{O_2}^+) \cdot x_{O_2}^a \quad (5.18)$$

This relation can then be used to express the oxygen molar fraction, $x_{O_2}^i$, at the oxygen analyser when extra oxygen is added but no fire gases are present.

$$x_{O_2}^i = \frac{\dot{V}_{O_2}^+ + \dot{V}_{O_2}^a}{\dot{V}} = \frac{\dot{V}_{O_2}^+ + (\dot{V} - \dot{V}_{O_2}^+) \cdot x_{O_2}^a}{\dot{V}} = \frac{\dot{V}_{O_2}^+}{\dot{V}} \cdot (1 - x_{O_2}^a) + x_{O_2}^a \quad (5.19)$$

From this equation, the ratio $\dot{V}_{O_2}^+/\dot{V}$ can be found

$$\frac{\dot{V}_{O_2}^+}{\dot{V}} = \frac{x_{O_2}^i - x_{O_2}^a}{1 - x_{O_2}^a} \quad (5.20)$$

and used in Equation (5.17)

$$\phi_2 = \frac{(1 - x_{O_2}^a)}{x_{O_2}^a \cdot (1 - x_{O_2}^a)} \cdot \frac{\dot{V}_{O_2}^+}{\dot{V}} = \frac{x_{O_2}^i - x_{O_2}^a}{x_{O_2}^a \cdot (1 - x_{O_2}^a)} \quad (5.21)$$

Finally, adding the results from step 1 and step 2, one ends up with

$$\phi = \phi_1 + \phi_2 = 1 - \frac{x_{O_2}^a}{x_{O_2}^a} \cdot \frac{(1 - x_{O_2}^a)}{(1 - x_{O_2}^a)} + \frac{x_{O_2}^i - x_{O_2}^a}{x_{O_2}^a \cdot (1 - x_{O_2}^a)} = \frac{x_{O_2}^i - x_{O_2}^a}{x_{O_2}^a \cdot (1 - x_{O_2}^a)} \quad (5.22)$$

Following this strategy and calculating the equivalence ratio using equation (5.22) means that the only measurements needed are oxygen mole fractions of ambient air ($x_{O_2}^a$), of the case with extra oxygen added but with ambient air at the inlet ($x_{O_2}^i$) and of the case with extra oxygen added and fire gases at the inlet (x_{O_2}), respectively.

To check the operation of the phi meter, a procedure of introducing different mixtures of methane, oxygen and nitrogen into the phi meter was carried out. For this pure methane ($\geq 99.95\%$) and a mixture of oxygen (16.00%) and nitrogen was used. By measuring the two separate flows, the theoretical ϕ could easily be calculated. The flows were mixed before reaching the phi meter, but no combustion took place except in the combustor of the phi meter. Since the aim was to study combustion where ϕ ranged from about 0.5 up to about 2.0, the phi meter was calibrated up to 2.25 (see Figure 5.2).

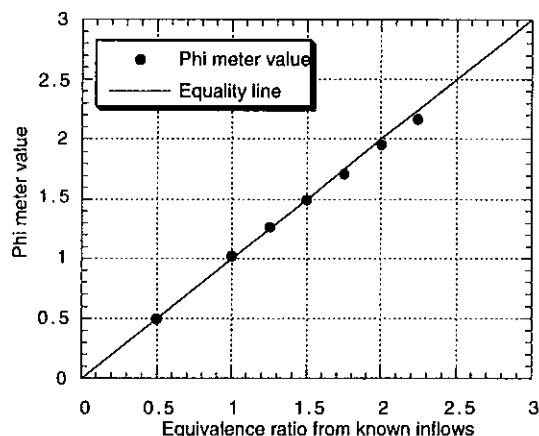


Figure 5.2 Comparison of the values of the equivalence ratio registered by the phi meter (calculated using Equation 5.22) with values calculated from known mixtures (flows) of methane and oxygen. No combustion took place prior to the phi meter.

The phi meter was originally constructed and calibrated for hydrocarbons, but some of the substances studied within this project contain atoms of other elements (nitrogen, sulfur and chlorine). Some exploratory experiments were therefore conducted, but no proof of un-accounted for influence by these elements have been found. For example, it was verified that the combustor did not convert HCl into Cl_2 (g).

Comparisons between values of the equivalence ratio measured with the phi meter and values calculated with Equation (5.4) do not show any systematic differences that could be attributed to the presence of heteroatoms in the molecule of the test substance.

There were differences, in some cases quite large, but they seemed to depend much more on the size of the opening. Only with the smallest opening, there are significant differences between the substances, but with that opening size there are also large differences within the same test and the burning conditions varied much between the tests. These results are presented in Figure 5.3 in the form of the ratio between the mass flow calculated from the measured ϕ and the mass flow calculated from temperature measurements. In Table 5.2 mean values of these numbers are presented.

From Figure 5.3 it can be seen that the deviation for PP (CH) were actually greater than for Ny (CHON) and TMTM (CHNS). Thus, the data suggest that the reasons for disagreements under small opening conditions do not lie in the presence of heteroatoms in the phi meter flow stream. Instead, they suggest a fluid dynamics or sampling issue.

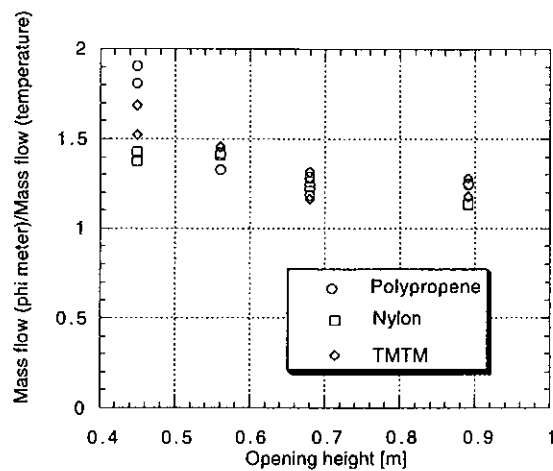


Figure 5.3 The ratio between the mass flow calculated from the equivalence ratio measured with the phi meter and the mass flow calculated from temperature measurements.

Table 5.2 Mean values of ratios between the mass flow calculated from the equivalence ratio measured with the phi meter and the mass flow calculated from temperature measurements.

Opening height / m	\dot{m}_ϕ / \dot{m}_T
0.89	1.20
0.68	1.24
0.56	1.40
0.45	1.62

The results in Table 5.2 suggest that if the phi meter values are correct, the temperature-based flow formulas underestimate the actual opening flow. Within the phi meter itself, extensive validation [15] has shown a vanishingly small discrepancy to the true ϕ value, when flows were accurately metered. Note, however, that those validations were based on known metered flows, not on sampling in a opening.

There are many possible explanations for the discrepancy obtained and, at the present time, we cannot fully assign its cause. One possibility is that despite the efforts made to take a representative sample, the sample in fact was somewhat non-representative.

This is difficult to assess. There have been some studies on flow patterns out of openings. However, the corresponding data on mixing of gases within the compartment is nearly totally absent. Thus, it cannot be readily evaluated whether the sampling in some way was biased.

Note that the discrepancy cannot be attributed to the approximation entailed in the temperature-based flow formulas. These formulas simplify matters by assuming that the hot gas layer has dropped to the floor level, whereas it will actually not go quite that low. The consequence is that if the post-flashover assumption is not quite fulfilled, the formula will OVER-estimate the opening flow. The data of Table 5.2, on the contrary, denote that either the phi meter results over-estimate air flow rates, or the temperature-based formulas underestimate it.

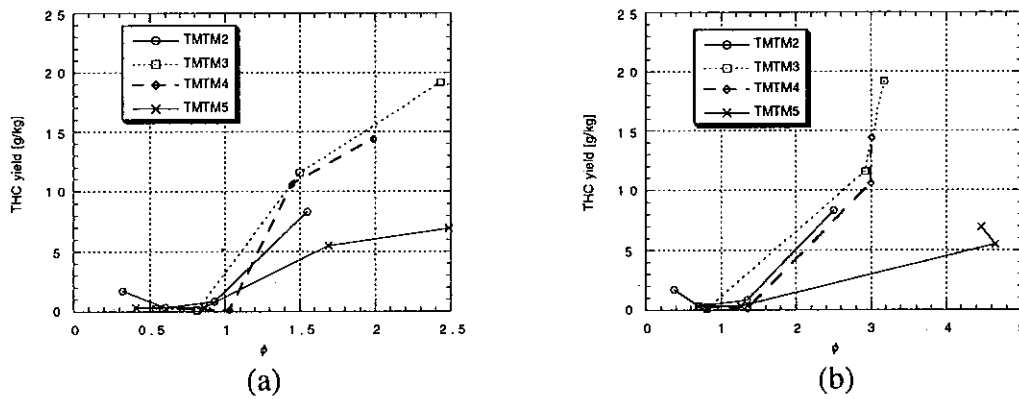


Figure 5.4 Comparison of THC yields for TMTM as functions of ϕ when ϕ is a) measured with the phi meter and b) calculated from the mass flow rate in the opening.

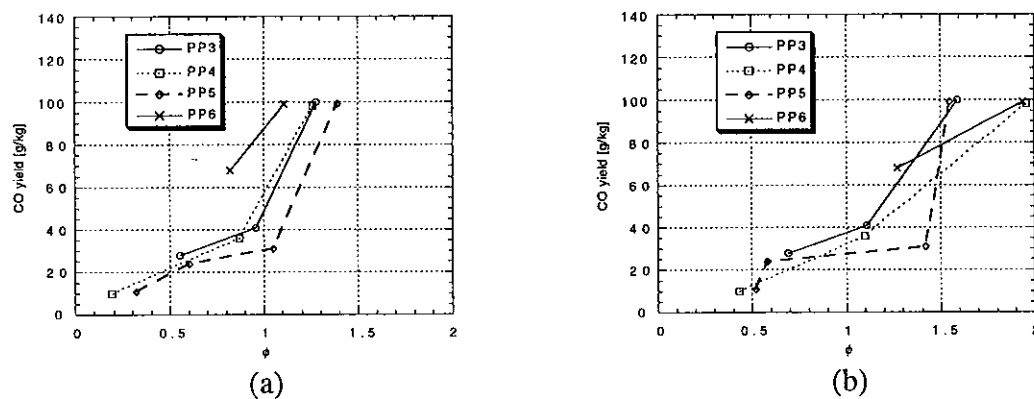


Figure 5.5 Comparison of CO yields for polypropene as functions of ϕ when ϕ is a) measured with the phi meter and b) calculated from the mass flow rate in the opening.

Comparing the measured ϕ with the measured volume concentration of carbon monoxide and THC show a very good agreement in such a way that when the

equivalence ratio passes 1, the concentrations of CO and THC increase considerably [16-19]. Making the same comparison using the equivalence ratio calculated from the computed mass flow does not show the same agreement, but suggests instead that the calculated ϕ value is too high (see Figure 5.4 and 5.5). Therefore the values measured with the phi meter have been used, when available, in the evaluation of the tests. For the tests CNBA4, CB3, CB4, CB5 and CB6 the calculated values have been used.

6 Opening sizes

To change the value of the equivalence ratio, ϕ , one can either change the MLR of the fuel or the inflow rate of oxygen or both. If steady state conditions are considered this corresponds to altering either the pool size or the opening size or both. For practical reasons it was decided to keep the pan size constant (for any given fuel) and only vary the opening size. After some screening tests a steady state heat release rate, HRR, of about 1000 kW seemed to be the value to aim for. For post-flashover compartment fires the inflow rate of air into the compartment, as shown in Chapter 4, can be estimated by Equation (4.1)

$$\dot{m}_{in} \approx 0.5 \cdot A \cdot \sqrt{h} \text{ kg/s}$$

where A is the area of the opening [m²] and h is the height of the opening [m]. In oxygen consumption calorimetry a value of 13.1 MJ of energy released per kg oxygen consumed (denoted with E) [20] is often used as a mean value for a large group of fuels. This together with

$$Y_{O_2} = \frac{M_{O_2} \cdot X_{O_2}}{M_{air}} = 0.231 \text{ kg } O_2 / \text{kg } air \quad (6.1)$$

where $X_{O_2} = 0.2095$ and the values of the molecular weights are taken from Table 9.1, gives a formula for estimating the HRR (stoichiometric):

$$\dot{Q} = E \cdot \dot{m} \cdot Y_{O_2} \approx 1.5 \cdot A \cdot \sqrt{h} \text{ MW} \quad (6.2)$$

This relation can then be used for finding the opening height that corresponds to a stoichiometric ($\phi = 1$) HRR of 1 MW.

$$h_{\phi=1}^{3/2} = \frac{2}{3 \cdot b} \text{ m}^{3/2} \quad (6.3)$$

b is the width of the opening [m]. If one wants to control the ventilation conditions with the opening height, one needs to find which mass inflow rate of air that corresponds to a certain opening height. This can be done in the following way:

$$\dot{m}_{\phi=1} = 0.5 \cdot b \cdot h_{\phi=1}^{3/2} \quad (6.4)$$

$$\dot{m}_{\phi=0.5} = b \cdot h_{\phi=1}^{3/2} \Rightarrow b \cdot h_{\phi=1}^{3/2} = 0.5 \cdot b \cdot h_{\phi=0.5}^{3/2} \quad (6.5)$$

$$\dot{m}_{\phi=1.5} = \frac{1}{3} \cdot b \cdot h_{\phi=1}^{3/2} \Rightarrow \frac{1}{3} \cdot b \cdot h_{\phi=1}^{3/2} = 0.5 \cdot b \cdot h_{\phi=1.5}^{3/2} \quad (6.6)$$

$$\dot{m}_{\phi=2} = \frac{1}{4} \cdot b \cdot h_{\phi=1}^{3/2} \Rightarrow \frac{1}{4} \cdot b \cdot h_{\phi=1}^{3/2} = 0.5 \cdot b \cdot h_{\phi=2}^{3/2} \quad (6.7)$$

Solving the equations above for the different opening heights, with b fixed as 0.8 m, gives the result presented in Table 6.1.

Table 6.1 Estimated opening heights, h , corresponding to a certain value of the equivalence ratio with b as 0.8 m and HRR as 1000 kW.

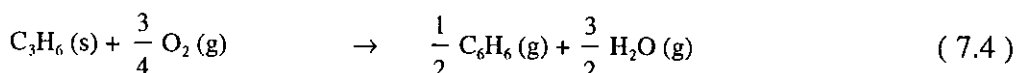
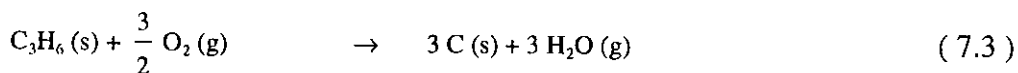
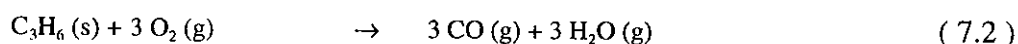
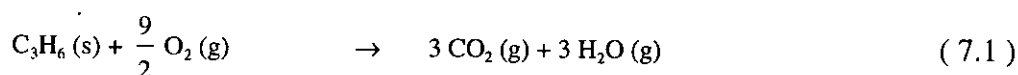
Expected ϕ	Estimated h / m
0.5	1.41
1.0	0.89
1.5	0.68
2.0	0.56

Based on preparation tests and the results from the first tests in the main series of tests, it was decided to perform some tests with an even smaller opening (0.45 m) and not to use the largest opening (1.41 m).

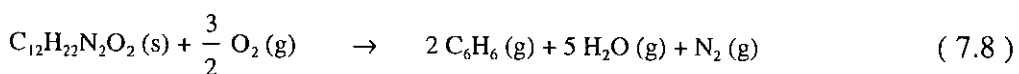
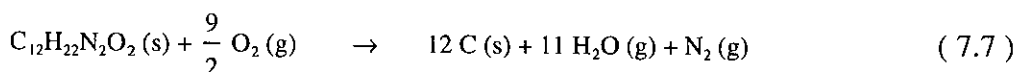
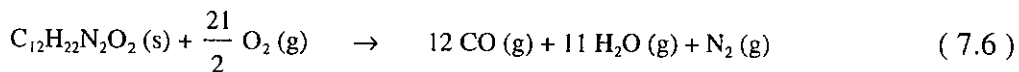
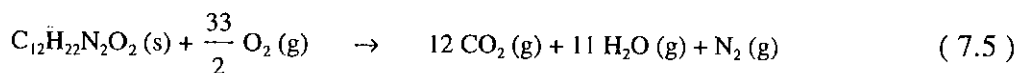
7 Chemical reactions

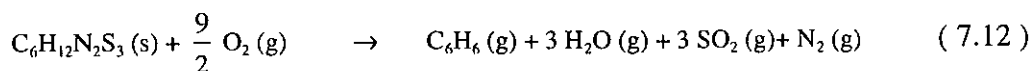
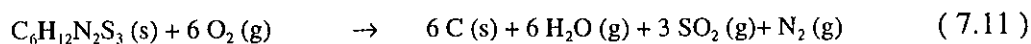
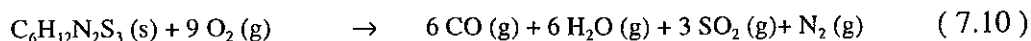
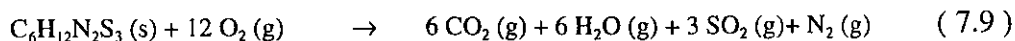
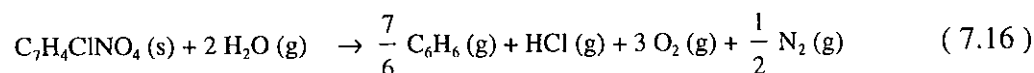
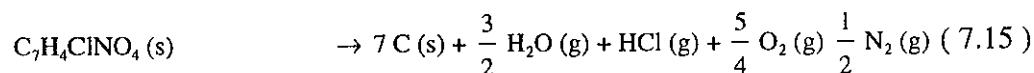
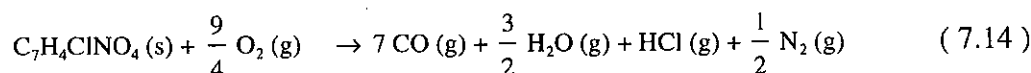
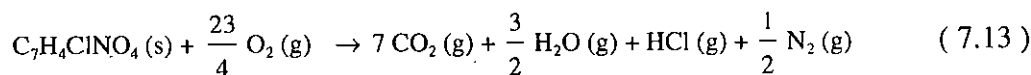
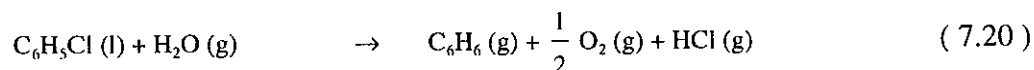
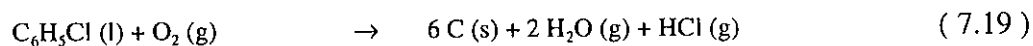
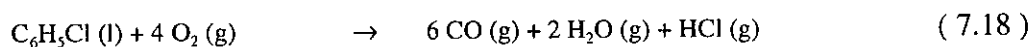
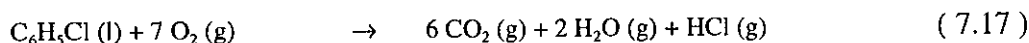
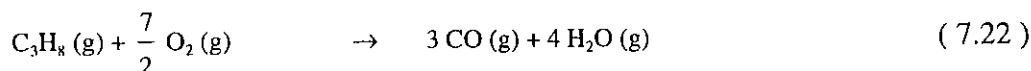
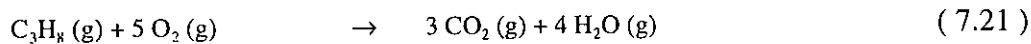
To be able to calculate the heat release rate by means of the production of carbon compounds instead of using oxygen consumption calorimetry (see Chapter 9), development of a calculation strategy was needed. For each substance used as fuel, four different reaction formulas were formed giving CO_2 , CO , C and C_6H_6 (THC), respectively. In an actual fire situation, THC include many different products (*e.g.* alkanes and aromatic compounds), but it is impossible to take into account all of them. Since benzene is one of the principal components of the smoke gases [21, 22], it was chosen to represent the THC. All products but for pure carbon (graphite) were assumed to be gaseous. This relates to the term Net Heat of Complete Combustion [23] when the product H_2O is assumed to be in the vapour state. In cases where the original substance contained elements other than carbon, hydrogen and oxygen it was assumed that sulfur formed SO_2 , nitrogen formed N_2 and chlorine formed HCl . These assumptions were needed to keep the variation in the reaction formulas only to the carbon compounds. The first five main compounds described in the equations below are the five substances used in the test series, propane was used for ignition and heptane and methanol are included as reference materials.

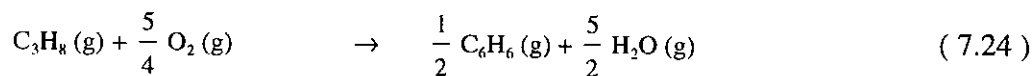
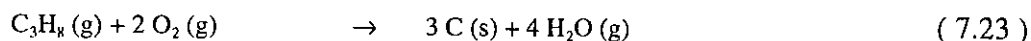
Polypropene



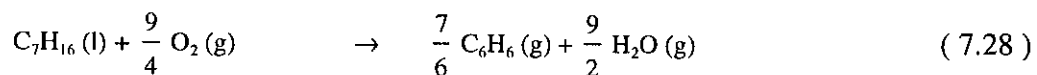
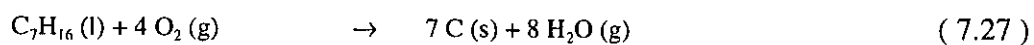
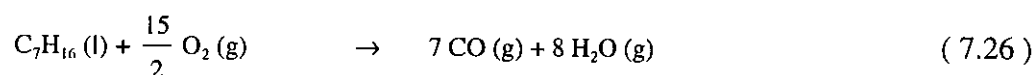
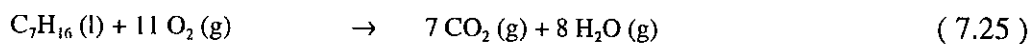
Nylon



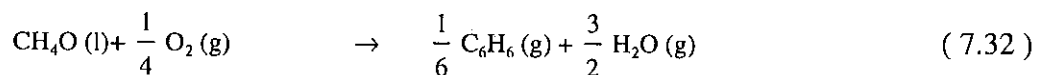
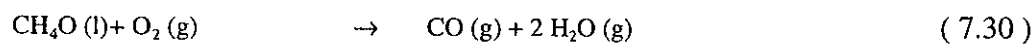
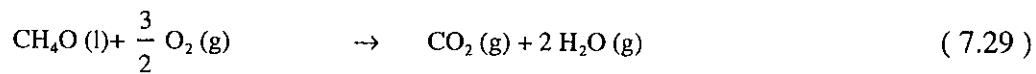
TMTM**CNBA****Chlorobenzene****Propane**



Heptane



Methanol



8 Compensation for the water removal in the carbon monoxide and carbon dioxide measurements

The IR-analyser used to detect CO₂ and CO in the duct needs completely dry sample gas and for that reason H₂O traps containing Drierite (active ingredient CaSO₄) were used. This means that the signals from the instrument correspond to the concentration of CO₂ and CO, respectively, in the dry gas and not to concentrations in the exhaust duct. Therefore a correction was needed. There were mainly three sources of H₂O: the ambient air, the combustion process and the water applicator (only in a few tests). In general the "wet" CO₂ mole fraction relates to the dry mole fraction in the following way.

$$x_{CO_2}^{dry} = \frac{n_{CO_2}}{n_{tot} - n_{H_2O}} = \frac{\frac{n_{CO_2}}{n_{tot}}}{1 - \frac{n_{H_2O}}{n_{tot}}} = \frac{x_{CO_2}^{wet}}{1 - x_{H_2O}} \Leftrightarrow \quad (8.1)$$

$$x_{CO_2}^{wet} = (1 - x_{H_2O}) \cdot x_{CO_2}^{dry} \quad (8.2)$$

where

$$x_{H_2O} = x_{H_2O}^a + x_{H_2O}^c + x_{H_2O}^w \quad (8.3)$$

The notations a, c and w stand for ambient, combustion and water application, respectively.

The mole fraction of H₂O in the ambient air can be written as [24]

$$x_{H_2O}^a = \frac{RH \cdot p_s(T_a)}{100 \cdot p_a} \quad (8.4)$$

where

RH = relative humidity [%]

$p_s(T_a)$ = saturation pressure of water vapour at T_a [Pa]

T_a = air temperature [K]

p_a = air pressure [Pa]

If the air temperature stays between 0 °C and 50 °C there exists a useful curve fit for p_s as a function of T_a [24]

$$\ln(p_s) = A - \frac{B}{T_a - C} \quad (8.5)$$

with the constants

$$\begin{aligned} A &= 23.2 \\ B &= 3816 \\ C &= 46 \end{aligned}$$

A combination of the two equations gives the final expression

$$x_{H_2O}^a = \frac{RH \cdot e^{\left[A - \frac{B}{T_a - C}\right]}}{100 \cdot p_a} \quad (8.6)$$

The contribution from the combustion depends on the substance used as fuel, the burning rate (the ventilation conditions, temperature etc.) and the compounds produced. To simplify the calculations, for a moment the assumption is made that a complete combustion with CO₂ as the only carbon product took place. This means that one can relate the production of H₂O to the production of CO₂ (the mole fraction in the wet combustion gases minus the mole fraction in the ambient air) in the following way

$$x_{H_2O}^c = a \cdot x_{CO_2}^{wet} \quad (8.7)$$

The water flow from the water applicator described above was 1 L/min in one test (PP5) and 2 L/min in the rest (Ny4, TMTM4, CB6). This volume flow corresponds to the molar flows 0.92 mol/s and 1.84 mol/s, respectively. The water was almost totally vaporised; not much water could be seen on the floor. As an approximation the values 0.8 mol/s and 1.6 mol/s respectively were used in the calculation, *i.e.* it was assumed that 87 % of the water from the water applicator reached the exhaust duct. Using this approximation the contribution from the water applicator can be expressed as

$$x_{H_2O}^w = \frac{\dot{n}_w}{\dot{n}_{tot}} = \frac{\dot{n}_w \cdot M_d}{\dot{m}_d} \quad (8.8)$$

where the subscript d refers to the conditions in the duct.

The final equation could be

$$x_{CO_2}^{wet} = (1 - x_{H_2O}^a - x_{H_2O}^c - x_{H_2O}^w) \cdot x_{CO_2}^{dry} \quad (8.9)$$

but this equation is not very useful for calculations since the combustion contribution contains the parameter that is wanted. Using Equation (8.7) and skipping some manipulating steps would lead to the following equation

$$x_{CO_2}^{wet} = \frac{(1 - x_{H_2O}^a - x_{H_2O}^w) \cdot x_{CO_2}^{dry}}{1 + a \cdot x_{CO_2}^{dry}} \quad (8.10)$$

This result can then be used for the correction of the CO measurements

$$x_{CO}^{wet} = (1 - x_{H_2O}^a - a \cdot x_{CO_2}^{wet} - x_{H_2O}^w) \cdot x_{CO}^{dry} \quad (8.11)$$

At this point it is interesting to compare the magnitude of the three different contributions. If the following values for the interesting parameters are used

$$\begin{aligned} \dot{n}_w &= 1.6 \text{ mol/s} \\ M_d &= 28.95 \text{ g/mol} \\ \dot{m}_d &= 3.8 \text{ kg/s} \\ RH &= 50 \% \\ T_a &= 293 \text{ K} \\ p_a &= 100 \text{ kPa} \end{aligned}$$

one finds that $x_{H_2O}^a = 0.0012$ and $x_{H_2O}^w = 0.012$ which means that the water application contribution is ten times the ambient air contribution. For the lower water flow the factor of course would be five instead. The contribution from the combustion is naturally not as easy to compare since that very much depends on the substance tested and the development of the fire, but one can see that in some cases the contribution from the fire was only half of the one from the air (CNBA1) and in some cases it was more than ten times as high as the contribution from the air (PP3, TMTM4).

9 Heat release rate

To characterize a fire, the HRR is one of the most important parameters and therefore it is important to be able to measure it. Only in a very well insulated system can a direct measurement of the heat transport in a flow be used to represent the total heat release. Such a scheme is called "sensible enthalpy" measuring and involves using recorded temperatures and handbook values of heat capacity in order to compute the enthalpy of the flow. Results with such an approach are unsatisfactory, if it is applied to real fire conditions, where the heat losses are significant. Instead different methods of using measured concentrations of the gases involved in the chemical reactions of the fire have been developed.

There are two common strategies of determining HRR: Oxygen Consumption (OCC) [7, 8, 24-26] and Carbon Dioxide Generation (CGC) [23]. The oxygen consumption calorimetry is the method most often used and also more frequently described and referred to in the literature. However, due to the fact that no oxygen measurements were available for the test series due to an O₂-instrument problem, it was decided to use carbon dioxide generation calorimetry instead. Since the test series included only a few fuels it was easier to develop a separate HRR formula for each substance than trying to find a universal formula that could be used in all cases. For under-ventilated experiments, when the combustion is far from complete, it is not enough to study the carbon dioxide generation only. Therefore, also the generation of carbon monoxide, soot and unburned hydrocarbons have been taken into account. The signals from the analyser measuring the molar ratios of CO₂ and CO were corrected in the way described in Chapter 8. The soot production, smoke production rate (SPR), was measured by a lamp/photo cell system described in ISO 9705 [6]. This parameter is called the instantaneous rate of light-obscuring smoke, R_{inst} , in the standard and is expressed in m²/s.

$$SPR = R_{inst} = k \cdot \dot{V}_d \quad (9.1)$$

where

$$k = \frac{1}{L} \ln \left[\frac{I_0}{I} \right] \quad (9.2)$$

and

\dot{V}_d = the volume flow in the exhaust duct [m³/s]

L = the length of the beam through smoky environment, *i.e.* the length of the diameter of the duct [m].

I_0 = the light intensity for a beam of parallel light rays measured without smoke with a detector having the same spectral sensitivity as the human eye [W/m²].

I = the light intensity for a parallel light beam having travelled a certain length through smoke [W/m²].

The SPR from Equation (9.1) has to be converted into a mass flow rate of soot. This requires a conversion factor which relates the m^2 of smoke produced to the kg of soot. The value of this factor varies between different fuels, but there was no information available about this factor for the substances of interest. Babrauskas and Mulholland, however, have presented data about the correlation between smoke and soot formation and from those values $10000 m^2/kg$ seems to be a good average [27].

The amount of unburned hydrocarbons reaching the measurement station was measured by a flame ionisation detector (FID) instrument calibrated against propane, but since benzene (C_6H_6) was chosen to represent all THC (see Chapter 7), the FID signal was converted to show the amount of benzene instead. For the fuels containing nitrogen, sulfur and/or chlorine the assumptions were made that: all nitrogen in the fuel is released as molecular nitrogen (N_2), the sulfur is released as gaseous sulfur dioxide (SO_2) and the chlorine is released as gaseous hydrogen chloride ($HCl(g)$). The development of the HRR formulas, based on Chapter 7, is described below.

9.1 Heats of combustion and heats of formation

To be able to calculate the contribution to the HRR from the production of each carbon compound according to the equations above (Chapter 7), the (net) heat of combustion, ΔH_c , for each equation was needed. The heat of combustion is defined as the enthalpy change for a complete combustion reaction where fuel reacts with O_2 to yield CO_2 and H_2O at a given temperature and pressure (298 K and 1 atm, respectively), *i.e.* the difference between the total enthalpy of formation of the products and the total enthalpy of formation of the reactants. Above, the word "net" in "net heat of combustion" means that it is assumed that the produced water is in the vapour phase. This assumption is used in equations and calculations throughout the report. If reactions, which are not complete combustion reactions, are to be studied, the more general ΔH_r (heat of reaction), which is applicable to all reactions, should be used instead. To find ΔH_r (including ΔH_c), the following expression is used.

$$\Delta H_r = \sum_{\text{products}} \Delta H_f - \sum_{\text{reactants}} \Delta H_f \quad (9.3)$$

Equation (9.3) is also used to find the heat of formation for a certain product from a known value of the heat of combustion. Table 9.1 presents values of ΔH_r and ΔH_c for the compounds taking part in the reactions described in the report. Most of the ΔH_f values are taken from the literature and then the ΔH_c values are calculated. In some cases ΔH_f was calculated from measured ΔH_c values (polypropene, Nylon 66) [2]. For CNBA no literature value could be found. Instead literature values [28-31] for similar compounds were used to calculate ΔH_c and this is described in reference 2.

Table 9.1 Heat of formation and net heat of combustion for different compounds (298 K) [28-33].

Name	Chemical formula	ΔH_f / (kJ/mol)	$\Delta H_c^{1)}$ / (kJ/mol)	$\Delta h_c^{1)}$ / (MJ/kg)
Oxygen	O ₂ (g)	0		
Nitrogen	N ₂ (g)	0		
Water	H ₂ O (g)	-241.826		
Carbon dioxide	CO ₂ (g)	-393.522		
Carbon monoxide	CO (g)	-110.527		
Carbon	C (s)	0		
Benzene	C ₆ H ₆ (g)	82.885		
Hydrogen chloride	HCl (g)	-92.312		
Sulfur dioxide	SO ₂ (g)	-296.842		
Polypropene	(C ₃ H ₆) _n (s)	-82.27×n	-1824×n	-43.34×n
Nylon 66	(C ₁₂ H ₂₂ N ₂ O ₂) _n (s)	-764.8×n	-6618×n	-29.24×n
TMTM	C ₆ H ₁₂ N ₂ S ₃ (s)	+658.6	-5361	-25.73
CNBA	C ₇ H ₄ ClNO ₄ (s)	-456.3	-2753	-13.66
Chlorobenzene	C ₆ H ₅ Cl (l)	+10.795	-2948	-26.19
Propane	C ₃ H ₈ (g)	-103.889	-2044	-46.35
Heptane	C ₇ H ₁₆ (l)	224.22	-4465	-44.56
Methanol	CH ₄ O (l)	-238.53	-638.6	-19.93

1) Net heat of combustion (H₂O (g))

When the heat of formation was found for all the compounds taking part in the equations presented in Chapter 7, ΔH_f for all these equations could be calculated as described in Equation (9.3). These ΔH_f values are presented in Table 9.2.

Table 9.2 ΔH_r for the 32 selected equations, where the ΔH_c values are printed in bold type.

Chemical reaction	Reaction number	ΔH_r / (kJ/mol)
Polypropene \Rightarrow CO ₂	(7.1)	-1824
Polypropene \Rightarrow CO	(7.2)	-974.8
Polypropene \Rightarrow C	(7.3)	-643.2
Polypropene \Rightarrow C ₆ H ₆	(7.4)	-239.0
Nylon \Rightarrow CO ₂	(7.5)	-6618
Nylon \Rightarrow CO	(7.6)	-3222
Nylon \Rightarrow C	(7.7)	-1895
Nylon \Rightarrow C ₆ H ₆	(7.8)	-278.6
TMTM \Rightarrow CO ₂	(7.9)	-5361
TMTM \Rightarrow CO	7.10)	-3663
TMTM \Rightarrow C	(7.11)	-3000
TMTM \Rightarrow C ₆ H ₆	(7.12)	-2192
CNBA \Rightarrow CO ₂	(7.13)	-2753
CNBA \Rightarrow CO	(7.14)	-772.4
CNBA \Rightarrow C	(7.15)	+1.274
CNBA \Rightarrow C ₆ H ₆	(7.16)	+944.4
Chlorobenzene \Rightarrow CO ₂	(7.17)	-2948
Chlorobenzene \Rightarrow CO	(7.18)	-1250
Chlorobenzene \Rightarrow C	(7.19)	-586.8
Chlorobenzene \Rightarrow C ₆ H ₆	(7.20)	+221.6
Propane \Rightarrow CO ₂	(7.21)	-2044
Propane \Rightarrow CO	(7.22)	-1195
Propane \Rightarrow C	(7.23)	-863.4
Propane \Rightarrow C ₆ H ₆	(7.24)	-459.2
Heptane \Rightarrow CO ₂	(7.25)	-4465
Heptane \Rightarrow CO	(7.26)	-2484
Heptane \Rightarrow C	(7.27)	-1710
Heptane \Rightarrow C ₆ H ₆	(7.28)	-767.3
Methanol \Rightarrow CO ₂	(7.29)	-638.6
Methanol \Rightarrow CO	(7.30)	-355.6
Methanol \Rightarrow C	(7.31)	-245.1
Methanol \Rightarrow C ₆ H ₆	(7.32)	-110.4

The values tabulated in Table 9.2 were used to obtain the final formulas for HRR. This is described in Section 9.2.

9.2 Heat release rate formulas

The basic principles in developing the different formulas were the same for all the substances and all the products even if the values of various constants differed.

$$\Delta h_{r,product} = \frac{\Delta H_{r,product}}{X_{product} \cdot M_{product}} \quad [\text{MJ/kg}_{\text{product}}] \quad (9.4)$$

X = number of moles produced of a product per mole substance consumed

M_{product} = molecular weight of product [g/mol]

$$\dot{m}_{product} = \frac{\dot{m}_{air} \cdot x_{product} \cdot M_{product}}{M_{air}} \quad [\text{kg}_{\text{product}}/\text{s}] \quad (9.5)$$

$$\dot{Q}_{\rightarrow product} = (-\Delta h_{r,product}) \cdot \dot{m}_{product} = \frac{(-\Delta H_{r,product}) \cdot \dot{m}_{air} \cdot x_{product}}{X_{product} \cdot M_{air}} \quad [\text{MW}] \quad (9.6)$$

For the reactions giving C_6H_6 as product the mole fraction figures from the FID instrument were divided by two since the FID was calibrated against propane which means that the signal corresponded to three carbon atoms. This can be written as

$$x_{\text{C}_6\text{H}_6} = \frac{1}{2} \cdot x_{\text{THC}} \quad (9.7)$$

where x_{THC} is the mole fraction of total amount of unburned hydrocarbons measured with the FID.

The values of M_{air} and M_{product} are presented in Table 9.3

Table 9.3 Molecular weights used in calculations [34].

Name	Chemical formula	Molecular weight / (g/mol)
Carbon dioxide	CO ₂	44.010
Carbon monoxide	CO	28.010
Carbon	C	12.011
Benzene	C ₆ H ₆	78.114
Oxygen	O ₂	31.999
Nitrogen	N ₂	28.013
Air (dry)	1)	28.964 ¹⁾
Polypropene	(C ₃ H ₆) _n	42.081 × n
Nylon 66	(C ₁₂ H ₂₂ N ₂ O ₂) _n	226.319 × n
TMTM	C ₆ H ₁₂ N ₂ S ₃	208.373
CNBA	C ₇ H ₄ CINO ₄	201.566
Chlorobenzene	C ₆ H ₅ Cl	112.558
Propane	C ₃ H ₈	44.097
Heptane	C ₇ H ₁₆	100.204
Methanol	CH ₄ O	32.042

1) To calculate the molecular weight for air, the following composition of dry atmospheric air has been used (content by volume): 78.084 % N₂, 20.946 % O₂, 0.934 % Ar, and 0.033 % CO₂ [35].

Using the constants tabulated above, one can calculate the four separate contributions for each substance resulting in the following formulas (the units of the numerical constants are MJ/kmol_{product})

$$\dot{Q}_{PP} = \frac{\dot{m}_{air}}{M_{air}} (607.9 \cdot x_{CO_2} + 324.9 \cdot x_{CO} + 214.4 \cdot x_C + 239.0 \cdot x_{THC}) \quad (9.8)$$

$$\dot{Q}_{nylon} = \frac{\dot{m}_{air}}{M_{air}} (551.5 \cdot x_{CO_2} + 268.5 \cdot x_{CO} + 157.9 \cdot x_C + 69.64 \cdot x_{THC}) \quad (9.9)$$

$$\dot{Q}_{TMTM} = \frac{\dot{m}_{air}}{M_{air}} (893.5 \cdot x_{CO_2} + 610.5 \cdot x_{CO} + 500.0 \cdot x_C + 1096 \cdot x_{THC}) \quad (9.10)$$

$$\dot{Q}_{CNBA} = \frac{\dot{m}_{air}}{M_{air}} (393.3 \cdot x_{CO_2} + 110.3 \cdot x_{CO} - 0.182 \cdot x_C - 404.7 \cdot x_{THC}) \quad (9.11)$$

$$\dot{Q}_{CB} = \frac{\dot{m}_{air}}{M_{air}} (491.3 \cdot x_{CO_2} + 208.3 \cdot x_{CO} + 97.79 \cdot x_C - 110.8 \cdot x_{THC}) \quad (9.12)$$

$$\dot{Q}_{propane} = \frac{\dot{m}_{air}}{M_{air}} (681.3 \cdot x_{CO_2} + 398.3 \cdot x_{CO} + 287.8 \cdot x_C + 459.2 \cdot x_{THC}) \quad (9.13)$$

$$\dot{Q}_{heptane} = \frac{\dot{m}_{air}}{M_{air}} (637.9 \cdot x_{CO_2} + 354.9 \cdot x_{CO} + 244.3 \cdot x_C + 328.8 \cdot x_{THC}) \quad (9.14)$$

$$\dot{Q}_{methanol} = \frac{\dot{m}_{air}}{M_{air}} (638.6 \cdot x_{CO_2} + 355.6 \cdot x_{CO} + 245.1 \cdot x_C + 331.2 \cdot x_{THC}) \quad (9.15)$$

where $Q_{substance}$ is in MW if \dot{m}_{air} is in kg/s and M_{air} in g/mol.

In the calculations, the value 28.964 g/mol (see Table 9.3) for the molecular weight of air was used. This value of course is calculated for ambient air without combustion, but since the flow in the exhaust duct and therefore the dilution of the combustion gases was high, this value is still a good approximation.

In the literature one can find constants tabulated describing heat released per mass O_2 consumed under complete combustion. Tewarson has also tabulated heat released per mass CO_2 and CO produced [23]. In Table 9.4 such compilation has been done for the values given from the equations above. These values are also compared with some values found in the literature [23, 36].

Table 9.4 Net heats of combustion per unit mass of oxygen consumed and carbon dioxide and carbon monoxide generated for the selected substances; comparison with values from the literature when available.

Substance	$\Delta h_{c,o_2}$ / (MJ/kg)			$\Delta h_{c,CO_2}$ / (MJ/kg)		$\Delta h_{c,CO}$ / (MJ/kg)	
	calc.	ref. 23	ref. 36	calc.	ref. 23	calc.	ref. 23
Polypropene	-12.67	-12.7	-12.62	-13.81	-13.8	-11.60	-11.7
Nylon ¹⁾	-12.53	-11.9	-12.30	-12.53	-13.3	-9.58	-10.8
TMTM	-13.96			-20.30		-21.80	
CNBA	-14.96			-8.94		-3.94	
Chlorobenzene	-13.16			-11.16		-7.44	
Propane	-12.78	-12.9	-12.78	-15.48	-15.3	-14.22	-14.0
Heptane	-12.69	-12.7	-12.68	-14.49	-14.5	-12.67	-12.8
Methanol	-13.31	-13.4	-13.29	-14.51	-14.5	-12.70	-12.9

1) The differences in the values for Nylon may be due to different types of Nylon.

10 Combustion efficiency

As mentioned above the HRR can be used to characterize a fire and the development of a fire. In a similar way the combustion efficiency, the ratio between the actual heat release rate and the heat release rate for complete (stoichiometric) combustion, describes the combustion process. For a certain fuel undergoing complete combustion, the stoichiometric heat release rate can be written as

$$\dot{Q}_{st} = \dot{m}_f \cdot (-\Delta h_c) \quad (10.1)$$

Using this relation and the computed value of the actual heat release rate, the combustion efficiency, χ , can be calculated with

$$\chi = \frac{\dot{Q}_{actual}}{\dot{Q}_{st}} = \frac{\dot{Q}_{actual}}{\dot{m}_f \cdot (-\Delta h_c)} \quad (10.2)$$

Table 10.1 Combustion efficiency (literature values) for different fuels [21, 23, 37]

Fuel	χ [23]	χ [37]	χ [21]
Methane	0.99	-	-
Propane	0.95	-	-
Propene	0.87	-	-
Methanol	0.96	0.96	-
Ethanol	0.92	-	-
Heptane	0.92	0.93	-
Benzene	0.69	-	-
Polythene	0.88	-	-
Polypropene	0.89	-	0.80
Nylon	0.88	-	1.00
PMMA	0.96	0.96	-
Polystyrene	0.69	0.44	0.65
Ethylbenzene	0.71	-	-
Propylbenzene	0.71	-	-
Chlorobenzene	-	-	0.58

For a fire, the combustion efficiency decreases with an increasing equivalence ratio but even in well ventilated fires the combustion efficiency is not equal to one. However, for some fuels it can be very close to unity, e.g. methane. In Table 10.1 the

combustion efficiency for different fuels are presented. Note that the values in the middle column are measured in either the Flammability Apparatus [23] or in the Cone Calorimeter [38, 39], but the values from Heskestad [37] and Månsson et al. [21] are from free burning pool fires. Some of the values presented in Table 10.1 are used to evaluate the validation tests described in Chapter 11.

11 Validation tests

To validate the equations presented above, measurements during tests with the industry calorimeter and the furniture calorimeter (used together with the ISO room) were used. The results from six validation tests, three with the furniture calorimeter (FC) and three with the industry calorimeter (IC), are presented in Table 11.1. Methanol and heptane were used as fuels. In all the tests the fuel was put in a pan, which was placed on a load cell. This made it possible to compare the calorimeter value with a value calculated from the mass loss using values of the heat of combustion from Table 9.1.

The results are presented as combustion efficiencies and the corresponding values calculated with oxygen consumption calorimetry (OCC) are presented for comparison. For the OCC, the values 13.3 MJ/kgO₂ and 12.7 MJ/kgO₂ have been used for methanol and heptane, respectively, as the net heats of combustion per unit mass of oxygen consumed. Literature values (see Table 10.1) are also included.

Table 11.1 Comparison between values of combustion efficiencies calculated for validation tests with the CGC and literature values. Values calculated with the OCC are also included.

Fuel	Calorimeter	χ_{CO_2}	χ_{O_2}	$\chi_{ref\ 23}$	$\chi_{ref\ 37}$
Methanol	FC	0.96	0.95	0.96	0.96
Methanol	FC	0.94	0.93	0.96	0.96
Methanol	FC	0.94	0.93	0.96	0.96
Methanol	IC	1.02	0.99	0.96	0.96
Heptane	IC	0.98	0.96	0.92	0.93
Heptane	IC	0.99	0.88	0.92	0.93

For the validation tests with the furniture calorimeter, the results from the CGC strategy agree very well with literature value. The situation is different with the industry calorimeter. Almost all the calibration values are higher than the values found in the literature, both with the CGC and the OCC. Only in the last test with heptane, there is a significant difference between the methods. Since also two of the values for OCC are higher than similar literature values, we presume that the explanation lies not in the uncertainties attached to the CGC strategy, but rather in experimental uncertainties.

One should also keep in mind that there exist many possible sources of error connected with these methods of determine the HRR and this is also described in the literature, *e.g.* in reference 9. Still the results in Table 11.1 indicate that the CGC strategy presented in this report is as good as the OCC and it should be better than the general OCC, where the approximation of 13.1 MJ of energy released per kg oxygen consumed is used [16].

12 Evaluation of chloronitrobenzoic acid

The substance CNBA burned only with difficulty by itself and the required HRR level and ventilation conditions were not reached at all. Therefore, non-woven polypropylene was added to the CNBA, distributed in separate layers (see Figure 11.1). In total 60 kg CNBA and 10 kg polypropylene was used.



Figure 12.1 In the test CNBA2 non-woven polypropylene was added to the CNBA, distributed in separate layers with polypropylene on top.

The added polypropylene increased the temperature inside the room and the burning rate, but it made the evaluation much more complicated since it was very difficult to say what was burning at a certain time. However, an effort was made by comparing the equivalence ratio measured with the phi meter and the equivalence ratio calculated using Equation (5.4) and the values in Table 5.1. The ϕ values have also been corrected with the opening size dependent mass flow factor (Table 5.2) to make the comparison easier.

The first strategy was to distribute the polypropylene over the whole burning period, *i.e.* during the test 1/7 of the burning mass was polypropylene (see Figure 12.1a). The calculated ϕ is too low before about 26 minutes and too high after that time. This led to the second step where it was assumed that all polypropylene was consumed before that time and only CNBA was burning in the later part of the test (see Figure 12.1b). Since the total mass loss during the first 26 minutes was 23.2 kg, the mass fraction of polypropylene in the fuel burned during this time period would in that case be 43.1 %. This gave a much better result and it is only for a short time period that a correction was needed.

The curves start to separate at 23.2 minutes and it was assumed that from this point the polypropylene fraction decreased to zero and the zero point was chosen to be at 29.5 minutes. It is now easy to find an equation for the straight line describing the decrease. During the time period 23.2 to 26 minutes 4.88 kg were burning which means that 2.10 kg (43.1 %) polypropylene should be distributed according to the straight line equation. Therefore, the equation was integrated and the constant in the equation was chosen to give a value as close as possible to these 2.10 kg. Now the results are close enough (see Figure 12.1c) to make it possible to study different yields, recoveries etc. [2]. The different steps can be combined in terms of MLR of polypropylene:

$$MLR_{PP} = \begin{cases} 0.431 \cdot MLR_{tot} & 0 < t < 23.2 \\ (1.993 - 0.0684 \cdot t) \cdot MLR_{tot} & 23.2 \leq t \leq 29.5 \\ 0 & t > 29.5 \end{cases} \quad (12.1)$$

The time used in Equation (12.1) and in Figure 12.1 was measured from the moment when logging of the data from the on-line instrument was started and not from ignition. The time for ignition was in CNBA2 3.12 minutes after measurement start.

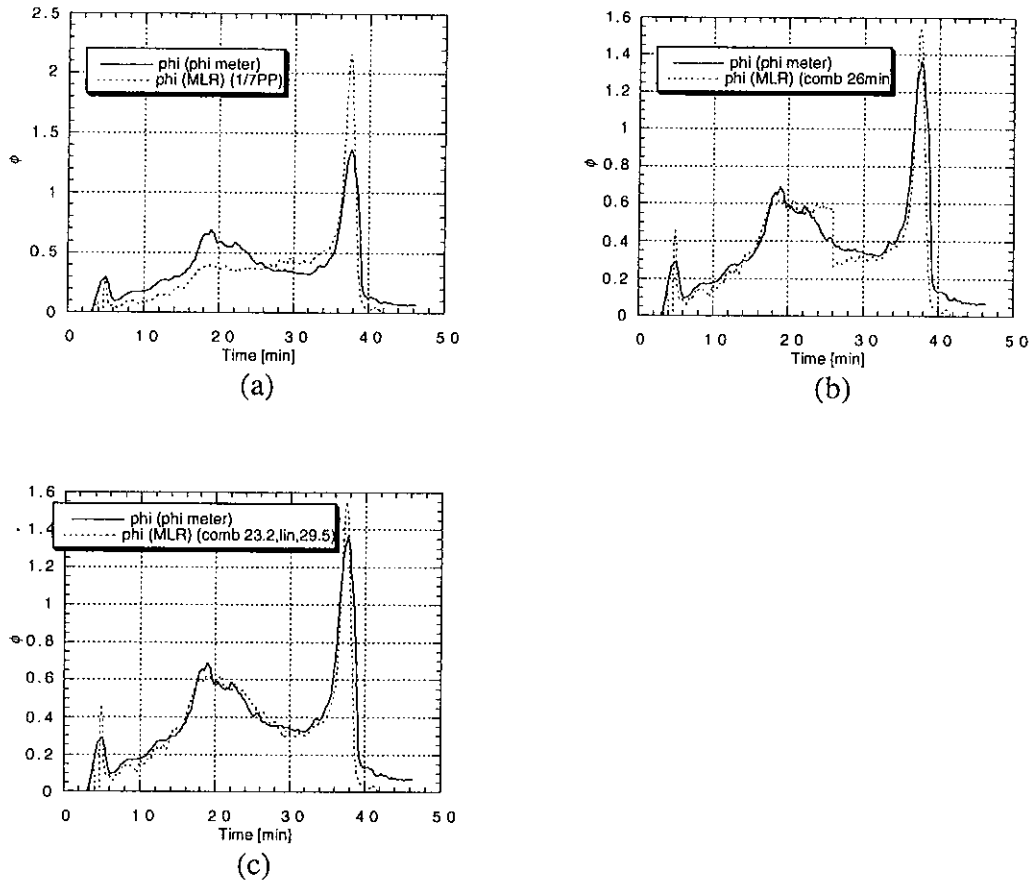


Figure 12.2 The three graphs describe the different steps in the way to find out when the in CNBA2 added polypropene was burning. The graphs represent different assumptions: (a) the burning of polypropene is distributed over the whole test, (b) all polypropene was burning during the first 26 minutes and (c) during the first 23.2 minutes the mass loss of polypropene was 43.1 % of the total mass loss; after that followed a time period when the polypropene fraction decreased to zero and after the time 29.5 minutes only CNBA was burning.

For the other two CNBA tests with added polypropene (CNBA3 and CNBA4), the first strategy was used (*i.e.* combustion of the polypropene was spread out over the whole burning period). This means that the approximation was made that 1/9 and 1/7 of the mass loss in the tests CNBA3 and CNBA4, respectively, was due to combustion of polypropene.

13 Conclusions

The main purpose with this report has been to develop and describe a way to calculate the heat release rate from fires. The oxygen consumption method is thoroughly investigated and also widely used, but in this case it was impossible to use due to the fact that no oxygen measurements were available for the test series due to an O₂-instrument problem. Instead it was decided to use carbon dioxide generation calorimetry. However, for under-ventilated experiments, when the combustion is far from complete, it is not sufficient to study the carbon dioxide generation only. Therefore, the generation of carbon monoxide, soot and unburned hydrocarbons have also been included. Since the test series included only a few fuels it was easier to develop a separate HRR formula for each substance than to try to find a universal formula that could be used in all cases. Validation tests (Chapter 11) showed that this method is as good as oxygen consumption calorimetry when the correct factor for the energy per kg oxygen consumed (E) was used and it should be better than the general OCC where a constant value, $E = 13.1$ MJ released energy per kg oxygen consumed, is used.

It should not be difficult to expand the theory to include other fuels provided the fuel is a well-defined substance with a known heat of combustion or heat of formation and a known chemical formula. It was not investigated whether it would be possible to derive a more general equation which would not require the fuel-specific computations that have been presented in this report. However, we can note that Equations 9.8 through 9.15 show some drastic variations in constants for different substances, thus any hopes for a simple formula are probably unrealistic.

Finally, we point out that carbon-generation methods for HRR are, in general, not applicable to substances which are composites or which show progressively different chemistry during the course of decomposition. Since wood is a substance which shows substantially different decomposition chemistry during early and late burning stages, it is probably unrealistic to expect to apply the method to many commodities of importance. By contrast, the oxygen consumption technique is successfully used for wood combustion, since the oxygen consumption constants are much less sensitive to the specimen composition.

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