INSTITUT FÜR BAUSTOFFE, MASSIVBAU UND BRANDSCHUTZ

MATERIALPRÜFANSTALT FÜR DAS BAUWESEN - MPA BRAUNSCHWEIG

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A Methodology to assess Species Yields of Compartment Fires by means of an extended Global Equivalence Ratio Concept

von

Burkhard Forell

Heft 198 · BRAUNSCHWEIG · 2007

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A Methodology to assess Species Yields of Compartment Fires by means of an extended Global Equivalence Ratio Concept

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by
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from Paderborn, Germany

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*) Either the German or the Italian form of the title may be used.

ABSTRACT

About 70 % of fire deaths occur by inhalation of smoke, whose toxicity is for the most part due to carbon monoxide (CO). The approach of correlating CO generation in compartment fires with ventilation conditions has become known as the global equivalence ratio concept (GER-concept). The review and partial re-examination of the principal research work on CO yields from compartment fires demonstrate the feasibility of this concept. The correlations of CO yields with the GER given by Gottuk and Lattimer from experiments in a hood and a prototype compartment are basically confirmed by additional results from large-scale experiments in the ISO 9705 room. However, for GER ≈ 0.5 and upper layer temperatures below 900 K, elevated CO yields which are not covered by Gottuk and Lattimer's low temperature correlation were partly observed.

The GER-concept is also validated by an examination of the flow dynamics in compartment fires, which showed that the ventilation conditions in the reaction zones, namely the fire plume and the upper layer, can be described by the GER. In addition to ventilation effects, which are of prime importance, vitiation effects were also studied. These become relevant when fuel is directly released into a vitiated upper layer. The particular case of pyrolysis of, for example, cellulosic fuels in vitiated upper layers leads to increased CO yields under well-ventilated conditions (GER < 0.25).

The GER-concept was extended to cover external combustion, both by flame extensions and in under-ventilated conditions. To assess the second phenomenon, an ignition criterion proposed by Beyler has been extended by taking into account the combustion efficiencies both inside the compartment and overall. This extended ignition criterion was in much closer accordance with the experimental data.

Regarding the efficiency of external combustion, which depends on the ventilation/vitiation conditions in the secondary control volume and the entrainment into the reaction zone, relatively little data is available. Gottuk and Lattimer proposed considering external combustion only when external flames reach into the unvitiated upper layer of an adjacent hallway. In contrast, Beyler's extended ignition criterion takes into account the reduced oxygen concentration and elevated temperatures in the secondary control volume, two factors which partially balance each other out.

Numerical fire simulation with the Fire Dynamics Simulator (FDS4) is of limited suitability for providing functional simulation results to be used for the GER-concept. Temperatures and mass flows for under-ventilated fires are not predicted with sufficient accuracy. For well-ventilated fires, the flame location, including the occurrence of flame extensions, can

be predicted with reasonable accuracy. Accurate prediction of external burning from under-ventilated conditions, however, lies beyond the capabilities of the FDS4 combustion model. As a remedy, FDS4 output data was post-processed to assess the ignitability of the exhaust gases by Beyler's ignition criterion. The applicability of this routine was demonstrated by a simulation of Gottuk's experiments.

The main asphyxiant species in compartment fires, apart from CO, are HCN and CO_2. In addition, oxygen depletion and the asphyxiating effects of irritants such as HCl, SO_2, and aldehydes contribute to the acute smoke toxicity, which can be quantified by toxicity models. Whereas yields of CO_2 and O_2 correlate well with the GER, the correlation of HCN yields is considerably influenced by additional parameters. It is concluded that in under-ventilated fires, smoke toxicity is significantly increased, and that the contribution of CO to the toxicity is also increased.

An extended methodology to derive the carbon monoxide source term of compartment fires is presented, which considers the GER of the primary compartment, the occurrence of external combustion, upper layer temperature effects, and fuel pyrolysis in the upper layer.

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I wish to dedicate this thesis to my parents
Johannes and Elisabeth-Charlotte Forell.

1 INTRODUCTION

1.1 Motivation

It is well known that in industrialised countries about seventy percent of the fatalities of accidental fires are from toxic fire effluents. This number has increased over recent years, which is attributed to the use of modern building products (Rasbach et al. 2004, Hall and Harwood 1995). Regarding the threat from toxic combustion products, fires can be classified into different categories:

- smouldering fires which produce relatively high toxic yields but have only very limited mass burning rates,
- free-burning fires and pre-flashover fires with increased burning rates but generally low toxic yields,
- post-flashover compartment fires, which pose a great threat due to high burning rates and possibly high toxic yields.

From US fire statistics between 1986 and 1990 it was revealed that about 70 % of structure fire deaths occurred in fires of the last category. Regarding the location of the victims, about 80 % of them died in locations adjacent to the room of fire origin. In fact 14 % of these cases the fire did not spread beyond the room of origin (Gann et al. 1994). From a review of catastrophic fires in places of entertainment a similar conclusion can be drawn. For most incidents with high death tolls the fire first developed in spaces other than the assembly room. Under these conditions large amounts of toxic effluents which were generated in under-ventilated fires spread into the assembly room (Forell 2004). Also for the assessment of plant safety, fully developed fires have to be considered to generate conservative source terms to be used in atmospheric dispersion models (Ortner and Hensler 1995).

The composition of fire effluents of fully developed compartment fires strongly depends on the ventilation conditions, whereas the chemical fuel structure is of minor importance (Babrauskas 1998). The state-of-the-art in describing the species yields of fully developed compartment fires is set by the “global equivalence ratio concept” (GER-concept) – a term first used by Pitts 1994, based on systematic work of Beyler in the middle of the nineteen-eighties.

1.2 Objectives of this work

In this thesis an extension of the global equivalence ratio concept is presented which is appropriate to calculate more realistic source terms for the production of gases in compartment fires. The use of time-dependent source terms for the heat release rate and the mass loss rate is common practice in fire safety engineering (Buchanan 2001, Hosser 2006). The source terms of toxic key species can be calculated from the mass loss rate using the species yields. With these data the spread of toxic fire effluents from a compartment fire can be analysed.

1.3 Structure of this work

After introducing the basic terms and correlations, some important findings from the literature are summarised. Different methods to determine the GER are described in the first part of this review. In the second part notable experimental studies dealing with the global equivalence ratio concept including all published large-scale studies are presented. For some studies significant amendments had to be made to the calculated equivalence ratio. The basic data and the test facilities described in the review chapter are referred to several times in the succeeding chapters of this thesis.

In Chapter 3 the results and open questions are considered in the light of the general understanding of compartment fire dynamics and plume theory. The scope of application of the GER-concept is embedded into the spectrum of compartment fires. Then characteristics of compartment fires without and with external combustion are discussed. This is done on the basis of data provided by Chapter 2 and additional studies.

The use of the state-of-the-art fire simulation model Fire Dynamics Simulator as an engineering tool to predict species generation is examined in Chapter 4. After introducing the CFD-model and notable validation work, the author’s fire simulation studies on some experiments described in Chapter 2 are presented. The restrictions of the combustion model are illustrated and a proposal for a remedy by post-processing of simulation output data is given.

Carbon monoxide is the dominating gas in fire smoke toxicity (Christian 1999, Babrauskas et al. 1998). Up to now the GER-concept was mainly applied for CO, since CO is a combustion intermediate of carbon-containing fuel. In Chapter 5 the question as to what extent the generation of other toxic key species can be correlated with the GER is also examined.

An extended methodology on the carbon monoxide source term of compartment fires is presented in Chapter 6.

2 THE GLOBAL EQUIVALENCE RATIO CONCEPT

2.1 Equivalence ratios

In compartment fires the compartment can be subdivided into a lower layer of incoming air and an upper layer of combustion products with excess air or excess fuel. The exchange of mass and energy between both layers is dominated by the buoyant fire plume that consists of the fuel gases, entrained air and combustion products. For steady state conditions the compartment's outflow equals the air inflow $\dot{m}_{air}$ plus the fuel mass flow $\dot{m}_f$. The GER is defined as the actual ratio of fuel mass flow to air mass flow divided by the respective ratio under stoichiometric conditions

$$\phi = \frac{\dot{m}_f / \dot{m}_{air}}{\left(\dot{m}_f / \dot{m}_{air} \right)_{stoic}} \tag{2-1}$$

The ratio $\left(\dot{m}_f / \dot{m}_{air} \right)_{stoic}$ is a fuel-dependent constant whose reciprocal is commonly termed the stoichiometric air/fuel mass ratio r_{air} or which is expressed by the stoichiometric oxygen/fuel mass ratio r_{O2}

$$r_{air,f} = \left(\dot{m}_{air} / \dot{m}_f \right)_{stoic} = r_{O2,f} / y_{O2}^{\infty} \approx r_{O2,f} / 0.233 \tag{2-2}$$

A GER smaller than 1.0 represents over-ventilated, fuel-lean conditions. Within this work, the frequently used term "well-ventilated" is used to characterise ventilation conditions which are comparable to open fires. A GER of 1.0 corresponds to stoichiometric conditions. A GER exceeding 1.0 represents under-ventilated, fuel-rich conditions. Within this work the term "vitiated" is used independently of the equivalence ratio for atmospheres with depleted oxygen concentrations.

When the plume is considered instead of a control volume, the mass flow through a horizontal cross section can be used to calculate a plume equivalence ratio (PER, Φ_{pl}), whose reciprocal is frequently termed the entrainment number N. At the interface height between the lower and the upper layer the PER is related to the GER (cf. Sect. 3.2.2.3). The equivalence ratio of the upper layer is the time record of the PER. A local equivalence ratio (LER, Φ_{loc}) can be defined for any location. For steady state conditions the average LER of well-mixed exhaust gases is used to represent the GER of the control volume.

2.2 General approach

In order to establish source terms for fire risk analysis, a suitable value to use is the species yield Y_i. The species yields are calculated by the mass of produced species divided by the mass of gasified fuel. Normalised species yields are calculated by the species yields divided by the maximum theoretical species yield from a certain fuel. Normalised yields $Y_{i,norm}$ are also termed generation efficiency.

To assess species yields by means of the GER a distinction must be made between

- products of complete combustion like carbon dioxide (CO_2), water (H_2O), and sulphur dioxide (SO_2),
- products of incomplete combustion like total hydrocarbon (THC), carbon monoxide (CO), and hydrogen (H_2), and
- the formation of hydrogen halides (HF, HCl, HBr, HJ).

The behaviour of the ideal normalised yield of products of complete combustion $Y_{cc,norm,id}$ in relation to the GER is

$$Y_{cc,norm,id} = 1 \quad \text{for} \quad \phi \leq 1 \quad \text{and} \tag{2-3a}$$

$$Y_{cc,norm,id} = 1/\phi \quad \text{for} \quad \phi \geq 1 \tag{2-3b}$$

The ideal depletion of oxygen $Y_{O2,norm,id}$ behaves the same as $Y_{cc,norm,id}$.

Thus the ideal normalised yields of total hydrocarbons $Y_{THC,norm,id}$ behave

$$Y_{THC,norm,id} = 0 \quad \text{for} \quad \phi \leq 1 \quad \text{and} \tag{2-4a}$$

$$Y_{THC,norm,id} = 1 - 1/\phi \quad \text{for} \quad \phi \geq 1 \tag{2-4b}$$

In real fires, where the assumptions of perfect mixing and infinite residence times are not valid, a deviation of the generation efficiencies from the ideal behaviour is found. Based on the oxygen depletion calorimetry, this deviation is related to the combustion efficiency (cf. (Hosser et al. 2000, Blume 2003, Will 2005)).

CO and H_2 are intermediate species of the oxidation of hydrocarbons to CO_2 and H_2O. Because of the importance of CO as a toxic key species (Christian 1999, Babrauskas et al. 1998), the main aim of the GER-concept is to predict the behaviour of the yields of CO in relation to the GER.

The formation of hydrogen halides by fuel decomposition is independent of the GER (Hartzell 1996).

2.3 Measurement techniques to determine the GER

To determine the GER of a certain control volume, the fuel mass flow $\dot{m}_f$ and the rate of ventilation of the compartment have to be known. For liquid and solid fuels, the fuel mass flow is typically measured by a load cell as mass loss rate. For gaseous fuels it is given by a controlled fuel supply rate. For quasi-steady state conditions, the rate of ventilation is either given by the air-inflow rate $\dot{m}_{in}$ or the outflow rate of exhaust gases $\dot{m}_{out}$ with

$$\dot{m}_{out} = \dot{m}_{in} + \dot{m}_f \tag{2-5}$$

Small and micro-scale experiments (Richter 1999, Markert 1996) and experiments in cone calorimeter chambers (Hietaniemi 1997, Hosser et al. 2000) were conducted with controlled air supply rate. Hood experiments (Beyler 1986a, Lim et al. 1984, Zukoski et al. 1991) were performed with controlled exhaust gas rate. It can be assumed that in these kinds of experiments the mass flows were obtained with reasonable accuracy.

In large-scale tests the compartments (Fig. 2-1) were free-ventilated. The air inflow becomes a function of the compartment fire dynamics and the geometry of the compartment and its vents. Hence, mass flow recordings have shown themselves to be a complex task and a potential source of errors which propagate in the calculations of the GER and the species yields. Among the large-scale experiments with flows through vertical vents which were reviewed, five different methods were used to determine the GER of the control volume. In four of these the GER calculation is based on mass flows through the opening, which were also calculated by different procedures.

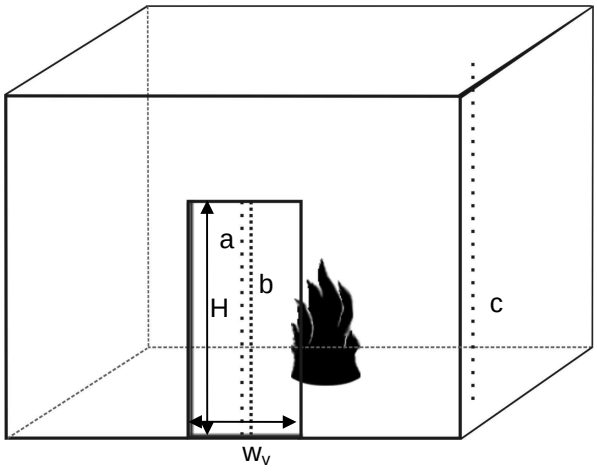

Fig. 2-1. Compartment with vertical vent of width w_v and height H. Thermocouple tree (a) or bi-directional pressure probes (b) in the doorway and thermocouple tree in the front corner (c).

2.3.1 Measurement by two thermocouple trees

A very common method to determine the mass flows through the vertical vent is by two thermocouple trees which are located in the doorway and in a quiescent front corner inside the compartment (Janssens and Tran 1992). The corner temperature profile $T_c(z)$ is used to calculate the pressure profile inside the compartment. The flow velocity profile v(z) is related to the pressure profile by Bernoulli's equation as

$$v(z) = \pm C_V \sqrt{2 \frac{\left| p_{comp}(z) - p_a(z) \right|}{\rho_v(z)}} \tag{2-6}$$

where $\rho_v(z)$ is the density profile calculated from the vent thermocouple tree under the assumption that the density of the out-flowing gas mixture is not substantially different from that of air of the same temperature. The orifice coefficient C_V is in the order of 0.7. The mass flows of inflow and outflow through a vent of the width w_v and the height H are calculated by integration over the elevation z

$$\dot{m}_{in} = \sqrt{2 \cdot g} \cdot \rho_{ref} \cdot T_{ref} \cdot C_{in} \cdot w_v \int_o^{Z_n} \left[\frac{1}{T_v(z')} \int_{Z'}^{Z_n} \left(\frac{1}{T_a} - \frac{1}{T_c(z'')} \right) dz'' \right]^{1/2} dz' \tag{2-7}$$

and

$$\dot{m}_{out} = \sqrt{2 \cdot g} \cdot \rho_{ref} \cdot T_{ref} \cdot C_{out} \cdot w_v \int_{Z_n}^{H} \left[\frac{1}{T_v(z')} \int_{Z_n}^{Z'} \left(\frac{1}{T_a} - \frac{1}{T_c(z'')} \right) dz'' \right]^{1/2} dz' \tag{2-8}$$

where the term $\sqrt{2 \cdot g} \cdot \rho_{ref} \cdot T_{ref}$ is a constant factor of 1570 kg*K*$m^{-2.5}$*s^{-1} resulting from the acceleration due to gravity, and the density of air at any referred temperature. Different orifice coefficients C_V for inflow and outflow may be used. However, it was found by Steckler et al. (1984) that the coefficient is quite insensitive to the heat release rate and the location of the fire. The neutral plane height z_n is found for steady state conditions under conditions of conservation of mass by Equation (2-5). This method was used by Bryner et al. (1994b) (cf. Sect. 2.4.4).

2.3.2 Measurement by one corner thermocouple tree

The method described above was simplified for the large-scale experiments in the ISO 9705 room within the TOXFIRE project (cf. Sect. 2.4.5). Lönnermark and Babrauskas (1996a) employed only a corner thermocouple tree and assumed a well-stirred

compartment with uniform temperature T_{comp} and uniform density ρ_{comp}. Therefore the integrals of Equations (2-7) and (2-8) can be solved directly giving

$$\dot{m}_{in} = \frac{2}{3}\sqrt{2 \cdot g} \cdot \rho_a \cdot C_{in} \cdot w_v \cdot z_n^{3/2} \sqrt{(1 - \frac{T_a}{T_{comp}})} \tag{2-9}$$

and

$$\dot{m}_{out} = \frac{2}{3}\sqrt{2 \cdot g} \cdot \rho_{comp} \cdot C_{out} \cdot w_v \cdot (H - z_n)^{3/2} \sqrt{(\frac{T_{comp}}{T_a} - 1)} \tag{2-10}$$

Lönnermark and Babrauskas used a uniform orifice coefficient of $C_V = 0.68$.

2.3.3 Measurement by a phi-meter at a representative location

The second method used by Lönnermark and Babrauskas (1996b) to determine the GER is based on the LER that was measured by a phi-meter at representative locations in the exhaust vent. The main parts of the phi-meter are a combustor, into which the fire gases and additional pure oxygen are introduced, and an oxygen analyser. As the combustor is preheated and equipped with a platinum catalyst, the combustion can be assumed as complete. The evaluation of the readings of the oxygen analyser is based on the assumption that only oxygen and nitrogen reach the oxygen analyser, other gases like water vapour and CO_2 have to be trapped before. Lönnermark and Babrauskas showed that the LER can be calculated from three oxygen mole fractions by

$$\phi_{loc} = \frac{X_{O2}^{i} - X_{O2}}{X_{O2}^{a} \cdot (1 - X_{O2})} \tag{2-11}$$

where

X_{O2}^{a} oxygen mole fraction in ambient air
X_{O2}^{i} oxygen mole fraction from ambient air with oxygen supply
X_{O2} oxygen mole fraction from fire gases with oxygen supply

2.3.4 Measurement by centreline thermocouples and bi-directional pressure probes

For their large-scale fire tests, Hosser et al. (2000) (cf. Sect. 2.4.6) employed a tree of thermocouples and bi-directional pressure probes on the centreline of the doorway (Fig. 2-1). The local density of the mixture was calculated by the thermocouple readings under the assumption that the density of the mixture is similar to the density of air. The difference

in dynamic pressure originating from the vent flow was measured by the bi-directional pressure probes. With this method the height of the neutral plane z_n can be found directly by interpolation of the data from different heights. The cumulative inflows and outflows are the sum of the partial flows $\dot{m}_{v,dA}$ through the areas $A_{v,dA}$ that were assigned to each probe. The partial flows are

$$\dot{m}_{v,dA} = A_{v,dA} \frac{C_v}{k_p} \sqrt{2 \cdot \rho_{dA} \cdot \Delta p} \tag{2-12}$$

The calibration factor was $k_p = 1.08$ (Emmons 2002). Hosser et al. also used the uniform orifice coefficient $C_V = 0.68$.

2.3.5 Measurement by an array of thermocouples and bi-directional pressure probes

Wieczorek (2003) (cf. Sect. 2.4.7) used an array of bi-directional pressure probes and aspirated thermocouples that were fixed in the compartment doorway. The calculation is similar to that described in Section 2.3.4. As the solution of the flow profile was improved, the mass flow could be calculated from the sampling nodes without introducing an orifice coefficient.

2.3.6 Expected mass flow

To provide a means to compare reported mass flows and resulting GERs, the expected mass flow through a vertical vent should be derived. It was shown before that the gas flow velocity through vertical vents is related to the temperatures inside and outside the compartment and the height of the opening H. Using the approximation that $\dot{m}_{in} = \dot{m}_{out}$ for well-developed compartment fires at steady state, the Equations (2-9) and (2-10) for inflow and outflow can be equated to yield the equation for the neutral plane height z_n, depending on the opening height and the temperatures inside and outside the compartment

$$z_n = H \frac{1}{1 + \left(T_{comp} / T_a \right)^{1/3}} \tag{2-13}$$

If Equation (2-13) is inserted into Equation (2-9), the air inflow

$$\dot{m}_{in} = w_v \cdot H^{3/2} \cdot C_v \cdot \frac{2}{3}\sqrt{2 \cdot g} \cdot \rho_a \cdot \sqrt{\frac{1 - T_a / T_{comp}}{\left(1 + \left(T_{comp} / T_a\right)^{1/3}\right)^3}} = w_v \cdot H^{3/2} \cdot K \qquad (2\text{-}14)$$

depends on the vent geometry (w_v, H), the orifice coefficient C_v, quasi-constant parameters (g, ρ_a), and a square root expression with the compartment temperature and ambient temperature. All factors except the vent geometry are summarised in the parameter K. With typical values (C_V = 0.68, g = 9.81 m/s^2, ρ_{air} = 1.21 Kg/m^3 at 293 K) this parameter depends on the compartment temperature and less on the ambient temperature. In Fig. 2-2 K = K(T_{comp}) is given for the whole range of compartment temperatures at two ambient temperatures of T_a = 283 K and T_a = 303 K respectively. For well-developed fires the upper layer temperature will always exceed 500 K. Hence, K can be taken as constant for practical use. It is seen that at higher temperatures, the decrease of the neutral plane height z_n, which is caused by thermal expansion of out-flowing gases, is compensated by increased flow velocity. Therefore, at elevated compartment temperatures the air flow through a vertical vent mainly depends on the vent geometry, and Equation (2-14) is typically used with K ≈ 0.52 kg/s*m$^{5/2}$ (Drysdale 1998, p. 331)

$$\dot{m}_{in} \approx 0.52\,\mathrm{kg/s} \cdot \mathrm{m}^{5/2} \cdot w_v \cdot H^{3/2} \qquad (2\text{-}15)$$

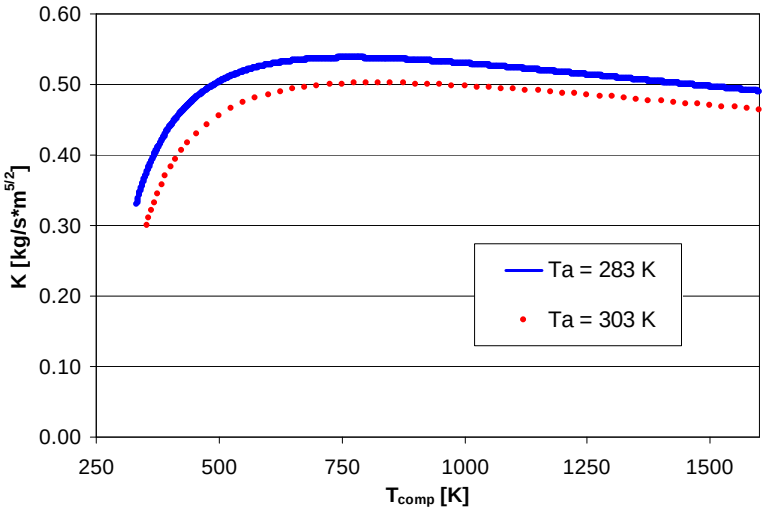

Fig. 2-2. The value of the parameter K of Equation (2-14) depending on the compartment temperature T_{comp} with C_V = 0.68.

The whole range of K is given from 0.40 kg/s*m$^{5/2}$ to 0.61 kg/s*m$^{5/2}$ (Fleischmann and Parkes 1997), depending on the orifice coefficient C_V. The dimensions w_V * H$^{3/2}$ are commonly summarised as the “ventilation factor” and Equation (2-15) is often termed as “Kawagoe-Equation” after the first researcher who recognised this relationship experimentally (Kawagoe 1958).

2.4 Extensive review of research under application of the GER-concept

Although there is a large amount of published data on species concentrations in fire gases, only very limited data is available about species yields. To calculate species yields, for a given control volume the mass flows of fuel and air or fire gases have to be known. To correlate species yields with ventilation conditions, quasi-steady state conditions are required which are difficult to obtain in large-scale fires with non-gaseous fuels. Therefore much research work has been done with gaseous fuels. Systematic data from liquid or solid fuels, which are of most importance in accidental fires, is very rare.

The test series were mainly conducted to represent dwelling fires where CO poses the greatest risk of intoxication. For this reason and because measuring CO concentrations is quite common for measurements of the heat release rate (ISO 1993, ISO 1999), carbon monoxide is by far the best examined toxic species. Another motivation was to derive source terms for risk assessment of chemical warehouse fires.

An exhaust gas collecting hood represents a prototype compartment where the expenses for the experimental setup are small and visual observations are possible. Therefore systematic work on the GER-concept started with hood experiments, where the hot gas layer under the hood was taken as the control volume. Then the work was extended to different scales of (prototype) compartments and later to compartments with attached hallways.

2.4.1 Beyler's hood experiments

The first systematic and most widely referenced work to correlate main species production and yields of buoyant diffusion flames with the equivalence ratio of an exhaust hood was done by Beyler (1983). His test apparatus (Fig. 2-3) consisted of three different gas and liquid burners, a gas collecting hood with an exhausting plenum and gas analysers for CO_2, CO, O_2, H_2O, H_2, and THC. The one metre diameter gas collecting hood was made of sheet metal insulated with ceramic fibreboard and a ceramic fibre blanket. It was exhausted by a circular lip in the vertical part of the hood. In his test series Beyler varied the height of the burner surface relative to the hood, the fuel supply rate, and the hood exhaust rate. At steady state conditions the hood exhaust rate was set so that the layer-to-air interface was below the exhaust lip and above the base of the hood to ensure that all gases leaving the hood were collected but no additional air was sucked in. Beyler calculated the equivalence ratio of the hood from the fuel supply rate and the hood exhaust rate. Using different modifications of propane burners, he found that species formation is independent of the flame structure but correlates with the equivalence ratio of

the hood (Fig. 2-4a-f). The maximum measured equivalence ratio was about 1.7. At this stage burning at the interface of the hood layer and ambient air started to occur (Beyler 1986a).

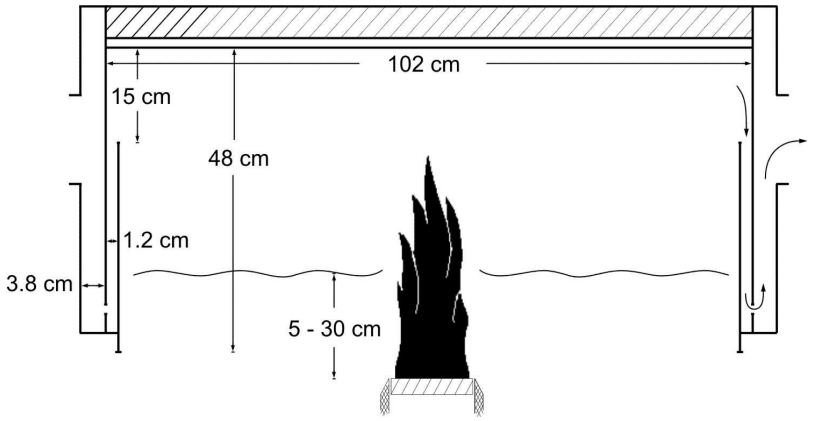

Fig. 2-3. Beyler's burner and cylindrical gas collecting hood (adapted from Beyler (1986a)).

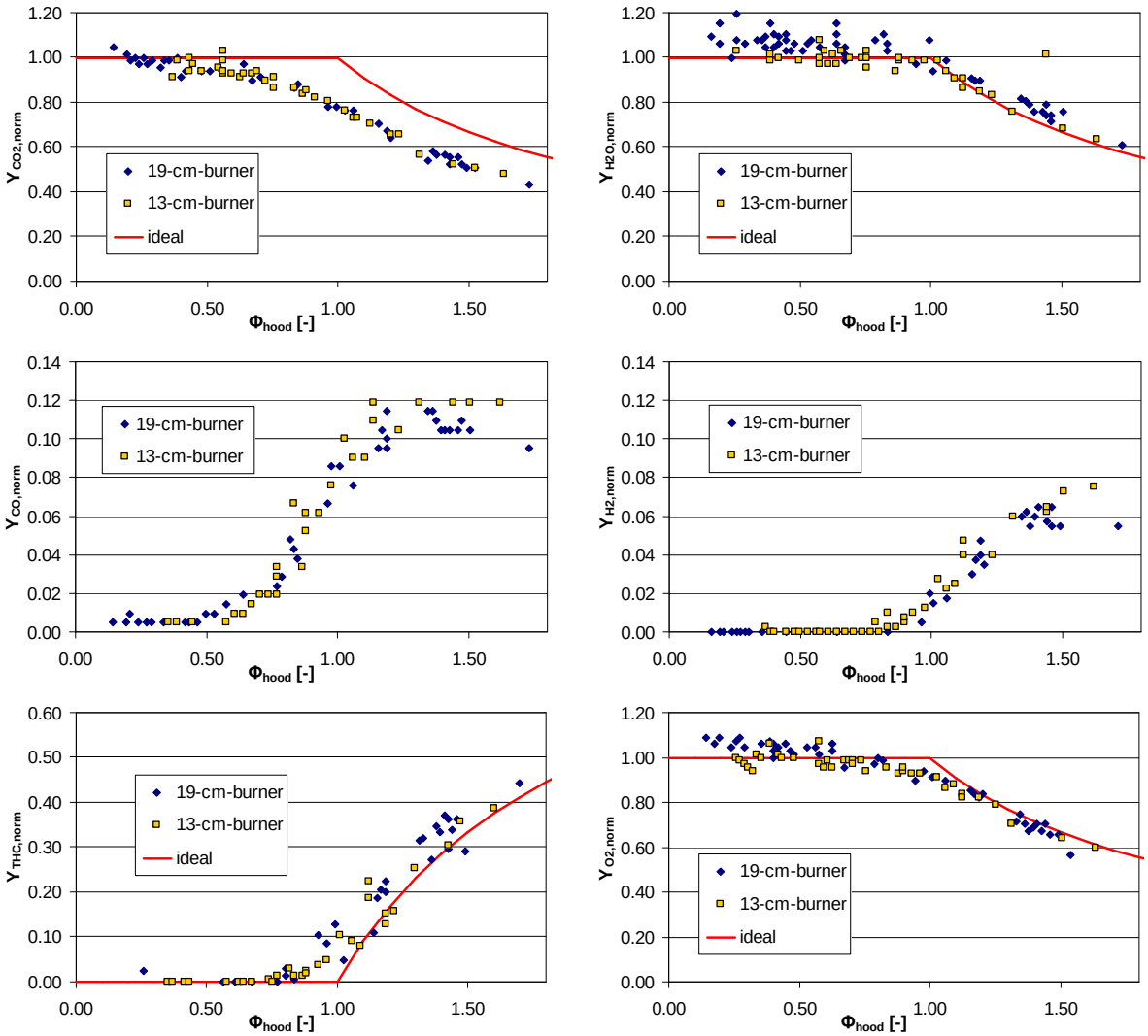

Fig. 2-4a-f. Normalised yields of measured chemical species as a function of the equivalence ratio for propane experiments using a 13 cm and a 19 cm burner with fuel supply rate corresponding to 8 – 32 kW ideal heat release rate (reproduced from Beyler (1986a)).

Additionally he developed a methodology to assess burning at the interface of the hood layer and the ambient air by introducing an ignition index (Beyler 1984, 2002)

$$I = \sum_{i=1}^{n} \frac{X_i \cdot \Delta H_{C,i}}{\int_{T_{mix}}^{T_{AFT,SL,i}} n_p \cdot c_p \cdot dT} \tag{2-16}$$

The ignition index is the sum of the ratios of the heat of combustion $X_i * \Delta H_{Ci}$ of the fuel species i of the hot layer gases (e.g. THC, CO, H_2) divided by the heat that can be taken up by the combustion products within the temperature interval of the mixing temperature T_{mix} of the stoichiometric mixture and the adiabatic flame temperature $T_{AFT,SL,i}$ of the stoichiometric limit mixture of the fuel species i. The value n_p is the number of moles of post-combustion mixture per mole of pre-combustion mixture. By definition, at $I \geq 1$ the condition for layer burning is given when a source of ignition is present. From his experiments Beyler (1984) reported layer burning when the ignition index exceeded 0.8 to 1.0. The ignition index is extensively treated in Sect. 3.3.1.3.

2.4.2 Hood experiments at the California Institute of Technology

Additional hood experiments with various modifications were conducted at the California Institute of Technology by co-workers of Zukoski and Kubota. Lim et al. (1994) used a natural gas burner under a hood of 1.2 m diameter at various burner-to-interface distances and fuel flow rates. For locations remote from the plume he found that species concentrations were independent from the location under the hood. It was hypothesised that chemical-equilibrium calculations might allow predictions for the observed mole fractions of CO and O_2 (Fig. 2-5a+b). For under-ventilated fires a reasonable prediction of the CO concentration curve would be obtained only for temperatures between 750 and 800 K. The increase of X_{CO} for $0.5 < \Phi < 1$ cannot be explained by the chemical equilibrium approach. Moreover the O_2 concentrations over zero cannot be predicted for $\Phi > 1$ (Fig. 2-5b). The comparison of data from different test series with different burners that result in different interface heights z_i, layer temperatures T_{ul}, and residence times t_{res} indicates that these parameters are either of minor importance compared to the equivalence ratio or that the combined effects of their variations on X_{CO} and X_{O2} incidentally balance each other out.

Additional experiments with improved gas analysing were conducted by Toner. Morehart used a larger hood (1.8 m square * 1.2 m tall) than Lim and Toner, that also allowed the injection of additional air into the hood atmosphere, well away from the plume, to decrease the hood equivalence ratio compared to the plume equivalence ratio. Morehart's

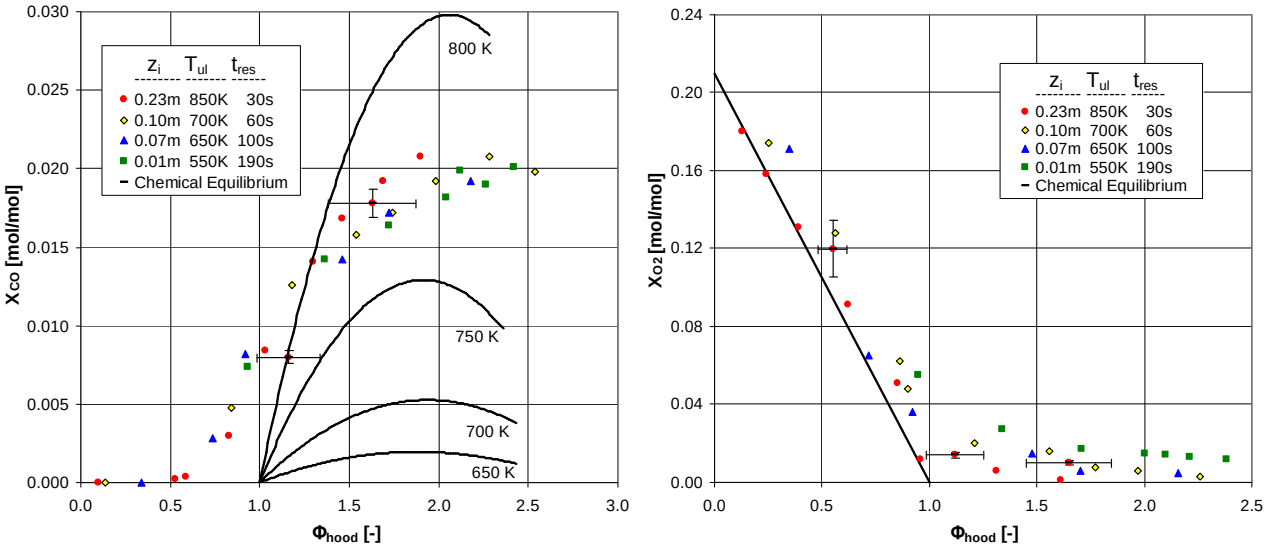

Fig. 2-5a+b. Mole fractions X_{CO} (a) and X_{O2} (b) observed in hood experiments as a function of the equivalence ratio. The solid lines represent the chemical equilibrium concentrations for the temperatures indicated (reproduced from Lim et al. (1994)).

results are reported as mass fractions in (Zukoski et al. 1991). For steady state conditions, these can be calculated to give species yields by

$$Y_{CO} = \frac{\dot{m}_{CO}}{\dot{m}_f} = \frac{y_{CO} \cdot \dot{m}_{out}}{\dot{m}_f} = \frac{y_{CO} \cdot \dot{m}_f \cdot (1 + r_{air}/\phi)}{\dot{m}_f} = y_{CO} \cdot (1 + r_{air}/\phi) \qquad (2\text{-}17)$$

and similarly

$$Y_{O2} = \frac{0.233 \cdot \dot{m}_{in} - y_{O2} \cdot \dot{m}_{out}}{\dot{m}_f} = 0.233 \cdot r_{air}/\phi - y_{O2} \cdot (1 + r_{air}/\phi) \qquad (2\text{-}18)$$

The normalised yields (Fig. 2-6a+b) from natural gas correlated well with the hood equivalence ratio and were apparently not influenced by the plume equivalence ratio. For comparison the figures also depict Toner's data that was obtained from a smaller hood at higher temperatures. For over-ventilated fires the combustion was consequently more complete than in Morehart's experiments, while at $\Phi > 1$ the formation of CO increased due to elevated temperatures.

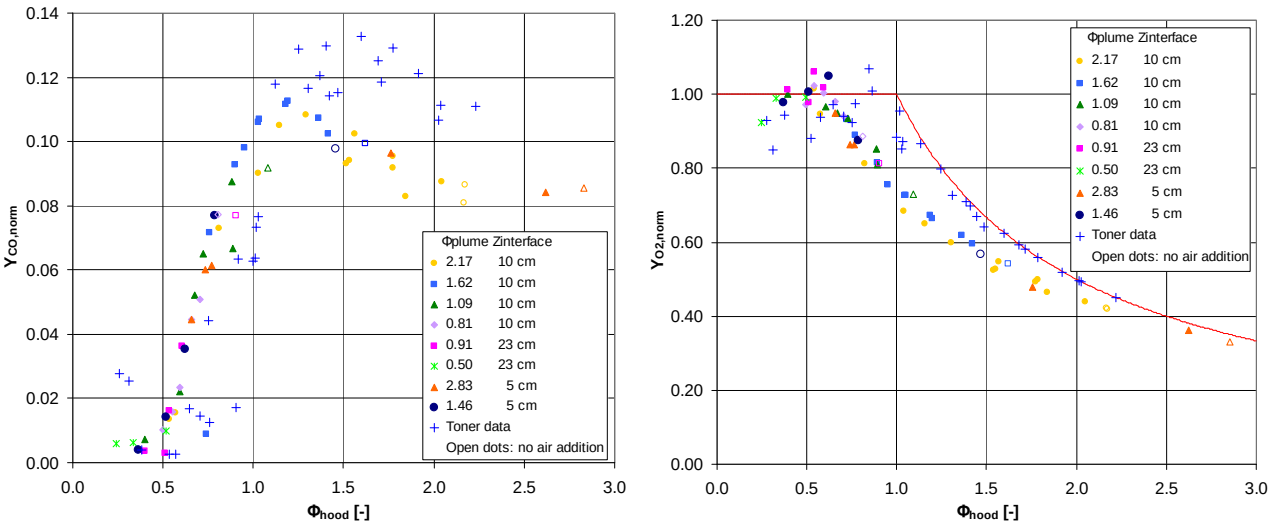

Fig. 2-6a+b. Normalised yield of CO (a) and depletion of O_2 (b) observed in Morehart's hood experiments as a function of the hood equivalence ratio. Open dots represent measurements without air addition ($\Phi_{pl} = \Phi_{hood}$) and filled dots represent measurements with air addition ($\Phi_{pl} > \Phi_{hood}$). Corresponding results of Toner are added for comparison (calculated from data of Zukoski et al. (1991)).

In order to investigate the temperature dependence of the species concentration, Morehart progressively increased the thickness of the hood insulation material. The calculated species yields from reported hood mass fractions of fuel gas CH_4, CO, and O_2 at equivalence ratios of 1.04 ± 0.05 and 1.45 ± 0.07 are shown in Fig. 2-7a-c and Fig. 2-8a-c, where Toner's corresponding data is also given.

For the nearly stoichiometric case (Fig. 2-7) the two data sets are reasonably consistent, especially for the decrease of CH_4 yields (a) and increase of oxygen depletion (c) with increasing temperature. The related combustion efficiency is also increased by increasing temperature. The decrease in the CO yields (b) is less evident at this equivalence ratio, as apparently different effects overlay in this temperature region. The use of different burner diameters within Morehart's experiments did not have major influence on the species yields.

In the under-ventilated case (Fig. 2-8) there is also a decrease of CH_4 yields (a) and increase of oxygen depletion (c) with rising temperature, while the CO yields (b) are indistinct. The clear temperature dependence, that was shown from chemical equilibrium calculations (cf. Fig. 2-5a), is not supported by the results of hood experiments.

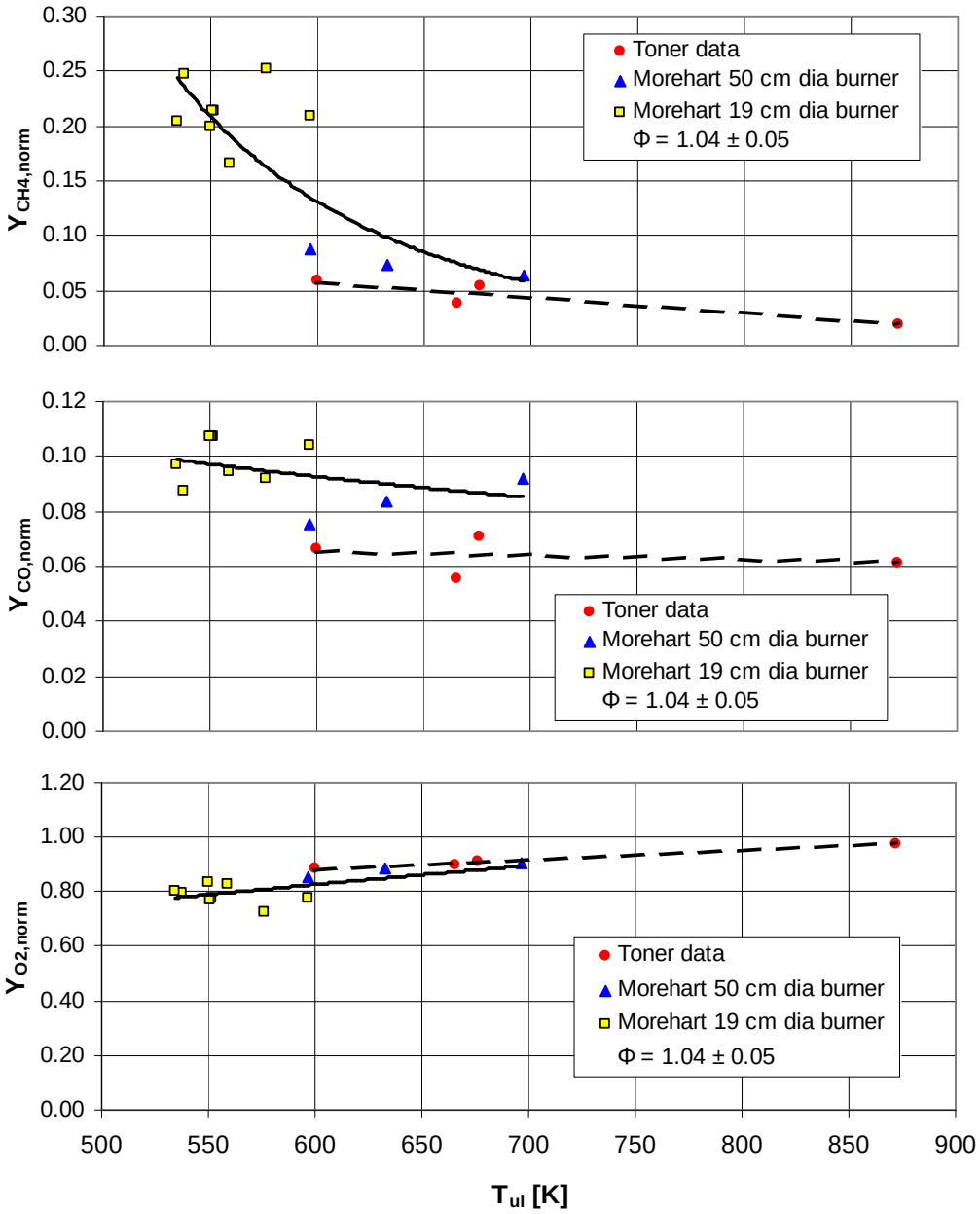

Fig. 2-7a-c. Normalised yields of CH_4 (a), CO (b), and O_2 (c) observed in Morehart's and in Toner's hood experiments as a function of the hood temperature at Φ of about 1.04. Curve fits by linear and power functions (calculated from data of Zukoski et al. (1991)).

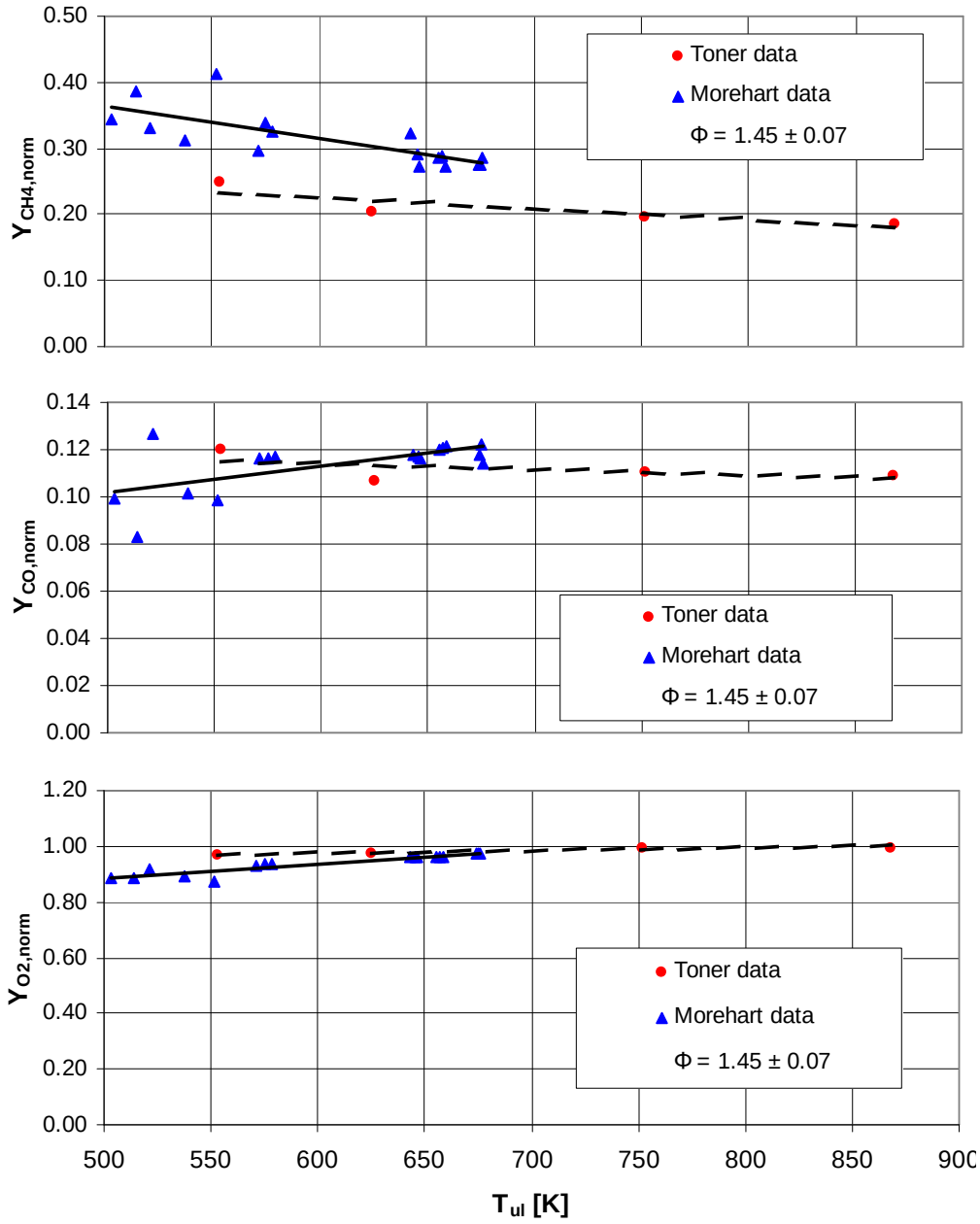

Fig. 2-8a-c. Normalised yields of CH_4 (a), CO (b), and O_2 (c) observed in Morehart's and in Toner's hood experiments as a function of the hood temperature at Φ of about 1.45. Curve fits by linear and power functions (calculated from data of Zukoski et al. (1991)).

2.4.3 Engineering methodology of Gottuk and Lattimer

A large series of room fire experiments with a prototype compartment, that partly had an adjacent hallway, was performed at the Virginia Polytechnic Institute and State University. First Gottuk (1992) used the insulated compartment constructed of steel, of l * w * h = 1.22 m * 1.52 m * 1.57 m (Fig. 2-9). The window-style exhaust vent was altered in size from 404 cm^2 to 1615 cm^2 with a constant 20 cm soffit. The inflow was naturally drawn

through a 0.305 m diameter duct via an air distribution plenum situated below the fuel pan. The air inflow was measured in the duct by a hot film velocity probe. Gottuk reported that inflow and outflow were separated in this compartment which was a result of the specific design of the inflow distribution plenum. Species concentrations and temperature indicated a reasonably well-mixed upper layer in this apparatus. Gottuk tested four fuels (hexane, PMMA, spruce, and flexible polyurethane foam) and measured species concentrations of CO_2, CO, O_2 and THC. The sampling probe projected 13 cm into the compartment through the centre of the exhaust window. Another sampling probe was located in the duct of the exhaust gas collecting hood to quantify the effect of external burning. Besides the experimental work Gottuk et al. (1995) examined the role of upper layer temperatures on CO production in compartment fires by a chemical kinetics model. They reported that for most situations upper layer temperatures below 800 K indicate chemically unreactive layers where combustion within the fire plume determines final CO production. Upper layer reactions should be taken into account from 900 K upwards.

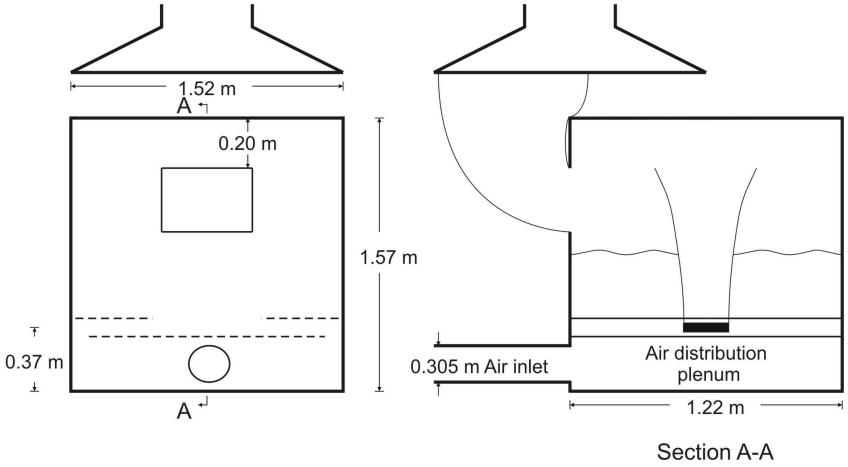

Fig. 2-9. Diagram of Gottuk's prototype compartment (adopted from Gottuk (1992)).

Additional research was performed by Lattimer et al. (1994) who focused on the species transport and oxidation within a hallway adjoining to the previous compartment (Fig. 2-10). The 3.66 m long insulated hallway could be equipped with soffits of different heights at the compartment-to-hallway interface and hallway-to-ambient air interface to study different conditions of external burning.

From their extensive research, Gottuk and Lattimer (2002) developed a complex engineering methodology for the prediction of species yields from compartment fires that is published in the SFPE-Handbook. They distinguish between two phenomena of external combustion. "Flame extensions" (Fig. 2-11a) occur when the fire plume or, if the fire plume impinges on the ceiling, the resulting ceiling jet is too long to fit in the compartment. This can happen in both over-ventilated and under-ventilated conditions. The second

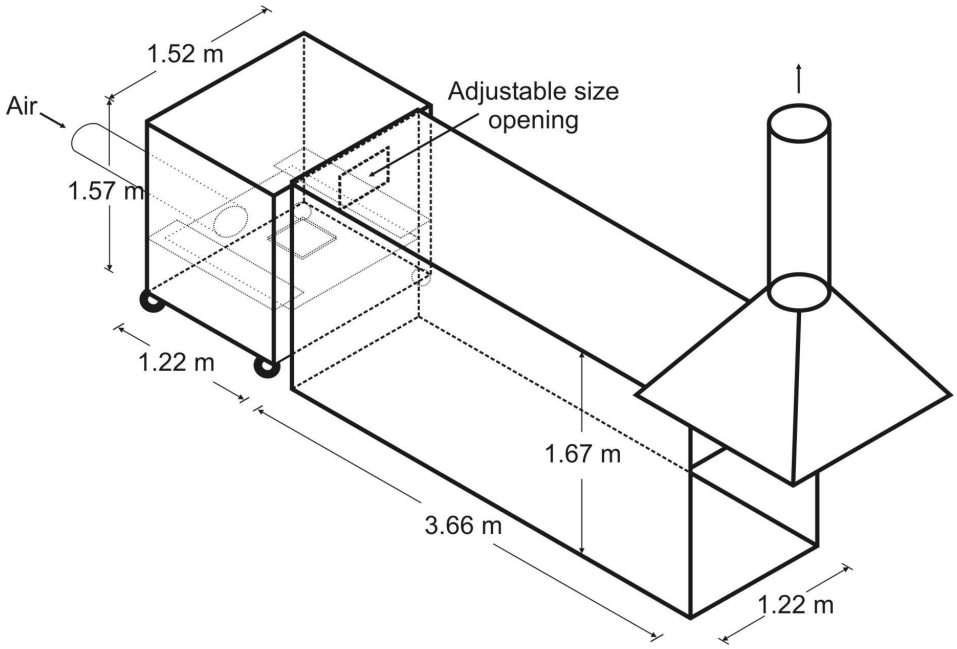

Fig. 2-10. Diagram of the prototype compartment with adjacent hallway (adopted from Lattimer et al. (1994)).

phenomenon they called “external burning” (Fig. 2-11b). “External burning” results from hot, fuel-rich exhaust gases that mix with air outside the compartment to create a secondary burning zone. Consequently this phenomenon can only occur during under-ventilated conditions. “External burning” can also be accompanied by layer burning which is the ignition of fuel-rich upper layer gases at the interface between lower and upper layer.

As “external burning” and “flame extensions” both mean combustion outside the control volume, within this work “external burning” in the sense of Gottuk and Lattimer is referred to as “external burning from under-ventilated conditions”, whereas “external combustion” is used as a genus for both phenomena.

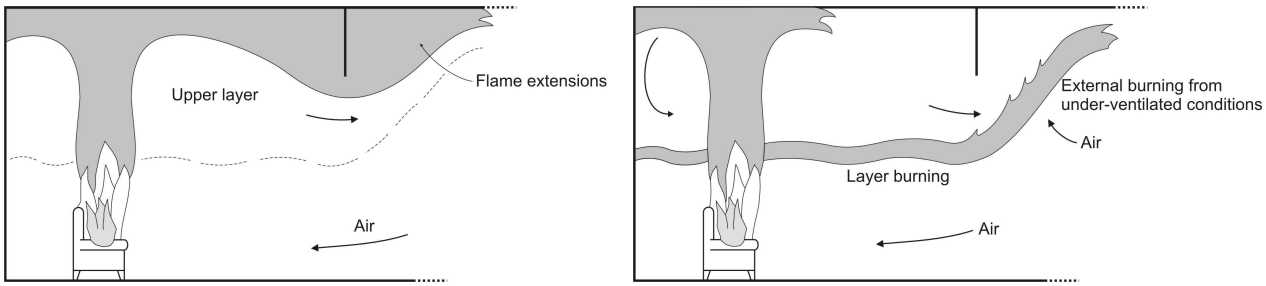

Fig. 2-11a+b. Illustration of external combustion as (a) flame extensions and as (b) external burning from under-ventilated conditions (adopted from Gottuk and Lattimer (2002)).

Within the engineering methodology (Fig. 2-12) the species yields are calculated through the correlation with either the GER of the primary compartment (Φ_{comp}) or the GER of a control volume that consists of the compartment and the adjacent space that is acquired by the external flame tip (Φ_{FT}) (Fig. 2-13). The engineering methodology starts with

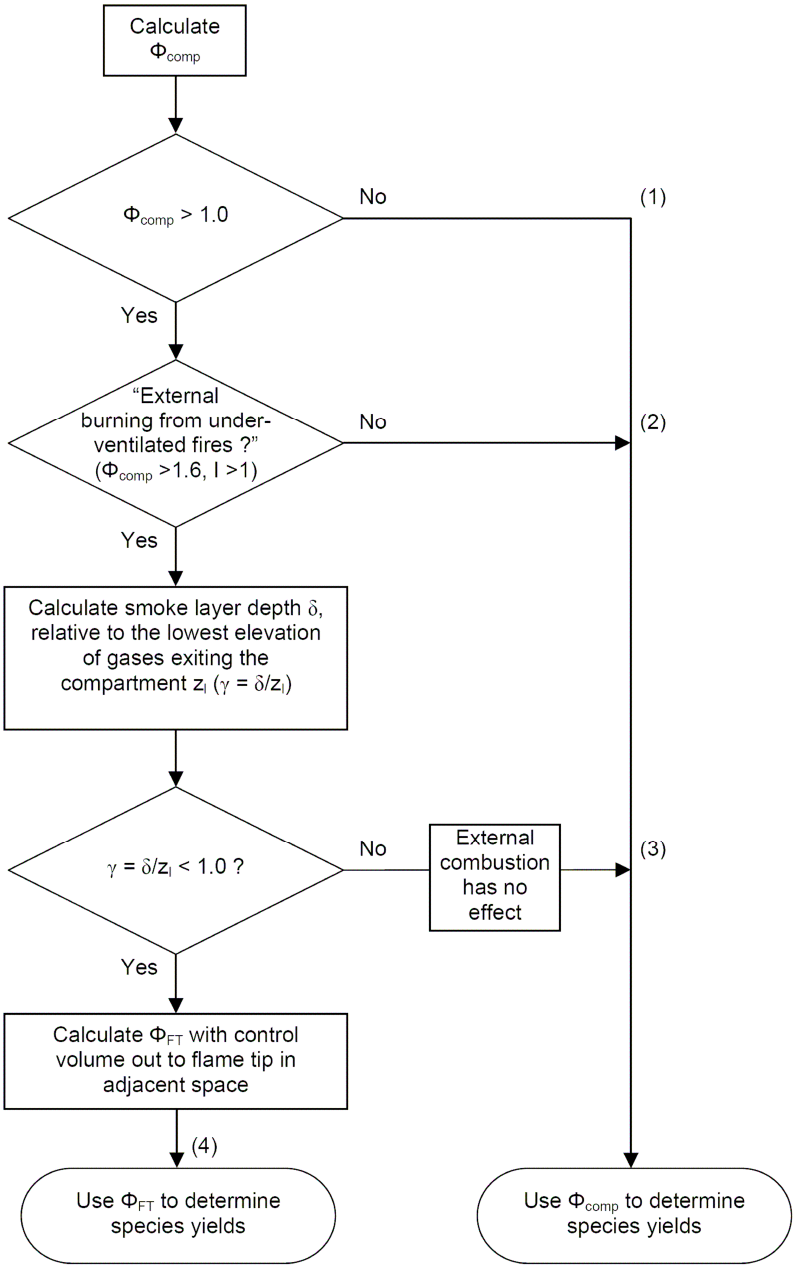

Fig. 2-12. Flow chart of Gottuk and Lattimer's methodology to determine the control volume for the relevant equivalence ratio (adapted from Gottuk and Lattimer (2002)).

determining the GER of the compartment. If $\Phi_{comp} < 1$ (1), the species levels are predicted by correlation with Φ_{comp}. If $\Phi_{comp} > 1$, a check needs to be made as to whether external burning from under-ventilated conditions does occur - otherwise Φ_{comp} will be used to calculate species yields (2). The recommended criteria to assess external combustion are either $\Phi_{comp} > 1.6$ or Beyler's ignition index (Equation (2-16)) for the exhaust gases. Flame extensions are not considered for external combustion. If external burning from under-ventilated combustion is predicted, the reduction of CO yields will be considered, if in addition the smoke layer depth δ is smaller than the lowest elevation of gases leaving the

compartment z_l (Fig. 2-13) (4). Then the length of the external flame tip has to be found together with the air mass flow $\dot{m}_{air,FT}$ that is additionally entrained outside the compartment. Consequently Φ_{FT} becomes

$$\phi_{FT} = \frac{\dot{m}_f \cdot r_{air}}{\dot{m}_{air,comp} + \dot{m}_{air,FT}} \tag{2-19}$$

Application of this equation is difficult, because no means are provided to calculate the air mass flow into the flaming zone outside the control volume.

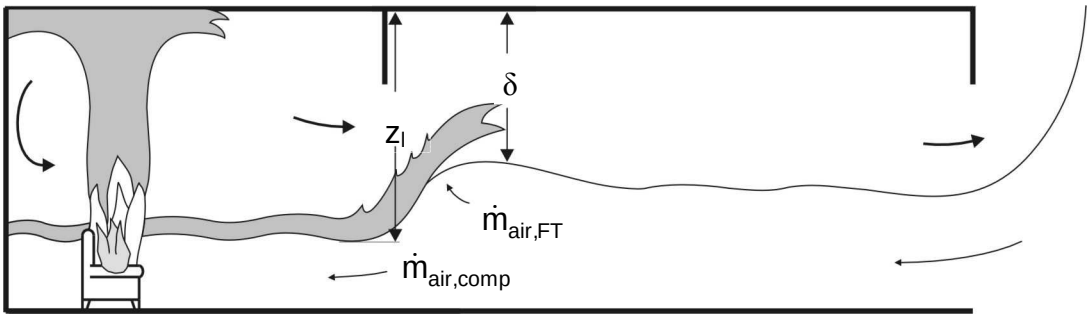

Fig. 2-13. Compartment and hallway configuration underlying Gottuk and Lattimer's engineering methodology. Note: the smoke layer depth δ and the elevation of gases leaving the compartment z_l are measured from the hallway ceiling.

When the control volume and the associated equivalence ratio are defined, the carbon monoxide yields can be calculated by one of two equations depending on the upper layer temperature (Fig. 2-14):

$$Y_{CO} = (0.19/180)\ \arctan(x) + 0.095 \qquad \text{for} \quad T_{ul} < 800\ K \tag{2-20a}$$

where x = 10(Φ – 0.8) and arcus tangent in degrees and

$$Y_{CO} = (0.22/180)\ \arctan(x) + 0.110 \qquad \text{for} \quad T_{ul} > 900\ K \tag{2-20b}$$

where x = 10(Φ – 1.25) and arcus tangent in degrees.

Equation (2-20a) represents the curve fit of Beyler's hood experiments for hexane (cf. (Beyler 1986a)). Equation (2-20b) is an approximate fit to hexane data from Gottuk's fires in the prototype compartment.

Gottuk and Lattimer noted that the methodology may not provide maximum levels of CO, although the equations had been shown to provide good results even for wood as a secondary fuel pyrolysing in the hot upper layer. Regarding the fuel, CO yields from hexane fires represent lower limits observed for different fuels. On the other hand, Gottuk and Lattimer (2002) decided to present un-normalised yields of CO in Equations (2-20a+b) as CO production is not strongly dependent on the fuel type.

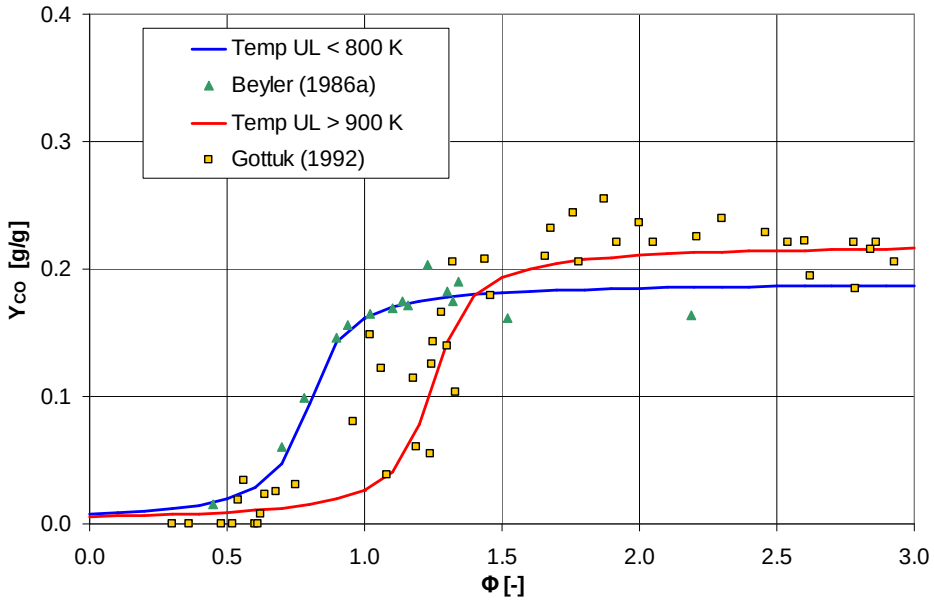

Fig. 2-14. CO yields according to the recommended Equations (2-20a+b) depending on the upper layer temperature. For comparison the experimental data of Beyler (1986a) and Gottuk (1992) is given (reproduced from Gottuk and Lattimer (2002)).

2.4.4 Pitts' algorithm for estimating CO formation

Based on hood experiments described above, his own chemical-kinetic calculations (Pitts 1994, 1995), and compartment fires in reduced and full-scale (Bryner et al. 1994a, b), Pitts (1997) specified four mechanisms of CO formation:

1) "Quenching of a turbulent fire plume upon entering a rich upper layer.

2) Mixing of oxygen directly into a rich, high-temperature upper layer with subsequent reaction.

3) Pyrolysis of wood in high-temperature, vitiated environments.

4) Approach to full-equilibrium combustion product concentration in a rich, high-temperature upper layer."

The first effect is of the greatest importance for fully developed fires and is considered in the GER-concept. The second effect was mainly concluded (Pitts 1997) from compartment fires conducted by Bryner et al. (1994a, b), where high concentrations of CO were found at the front of the enclosure. The mass flows of these tests were later (Pitts 2001, 2006) found to be under-estimated by a factor of the square root of 8 (≈ 2.8) resulting in an over-estimation of the GER. Although this insight partly invalidates the relevance of the second effect, Pitts (2006) recently confirmed these basic effects and suggested the use of discrete equivalence ratios for the plume, the upper layer and the compartment. The

engineering algorithm for estimating CO formation in enclosure fires (Fig. 2-15), which reflects the four mechanisms, remained unrevised after discovery of the square root of 8 mistake for the mass flows.

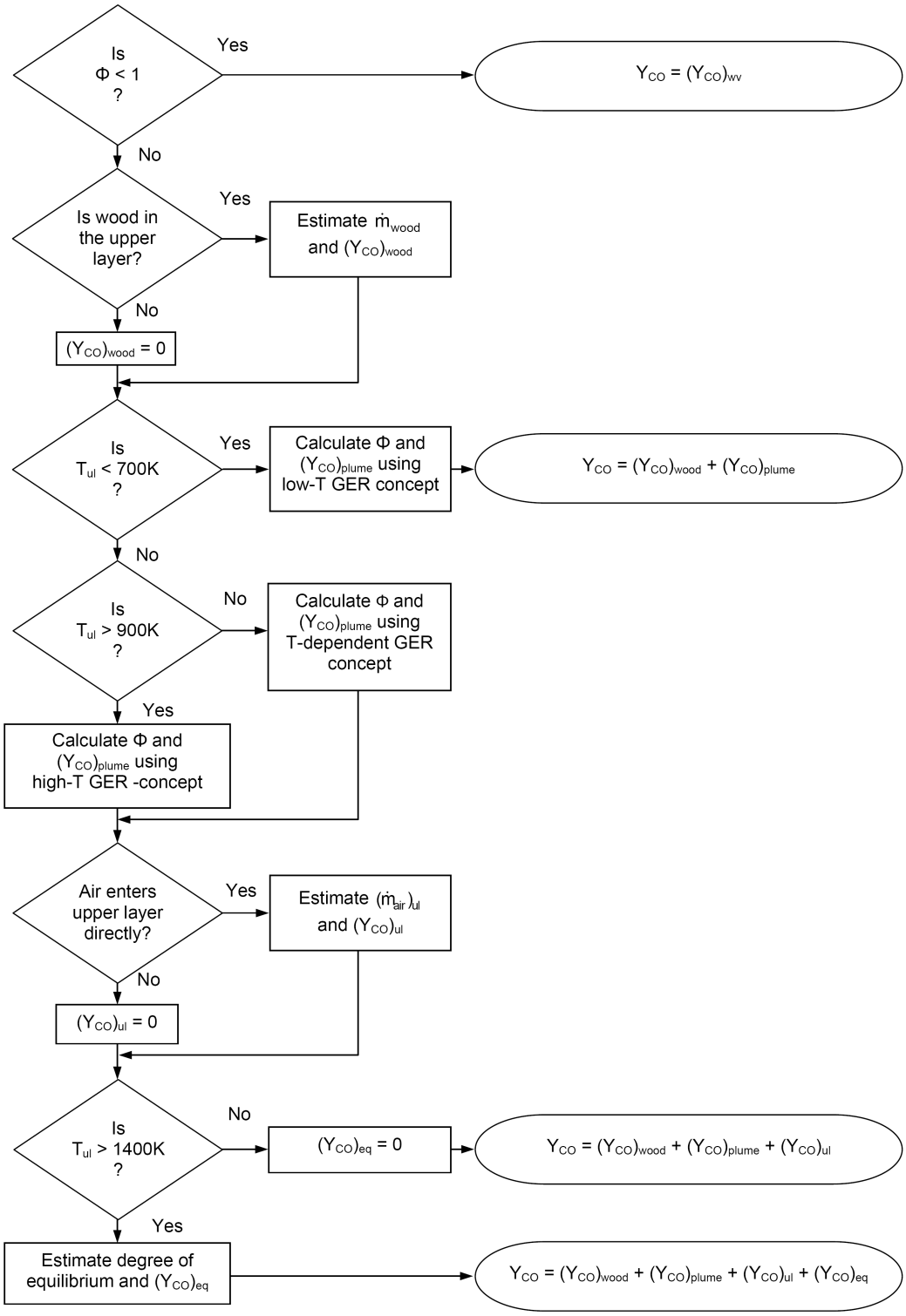

Fig. 2-15. Pitts' algorithm to predict CO generation in enclosure fires. Subscripts refer to the mechanism mentioned above: plume ->①, ul ->②, wood ->③, eq ->④ (adapted from Pitts (1997)).

Quantitative correlations do not exist in the context of this algorithm. It is remarkable that for the full range of over-ventilated conditions only a minimum CO production is assumed. For under-ventilated conditions, depending on the fire scenario, the CO yields of all four mentioned mechanisms are added together in this methodology. For under-ventilated fires, three discrete levels of the upper layer temperature ($T_{ul} < 700$ K, $T_{ul} > 900$ K, and $T_{ul} > 1400$ K) are concluded from chemical-kinetic calculations. As indicated in Fig. 2-16, under T_{ul} of 700 K upper layer reactions are not expected, therefore CO concentrations resulting from plume reactions are “frozen” (Pitts 2001). Above $T_{ul} = 900$ K, in accordance with Gottuk and Lattimer’s methodology (Sect. 2.4.3) a considerable reaction velocity has to be assumed also in the upper layer. Above $T_{ul} > 1400$ K the modelling results indicated that rich gas mixtures begin to approach thermodynamic equilibrium. At these high temperatures a slow conversion of H_2O and CO_2 to H_2 and CO is predicted to take place by the water gas shift reaction (Pitts 2001). CO consumption by external combustion is not considered.

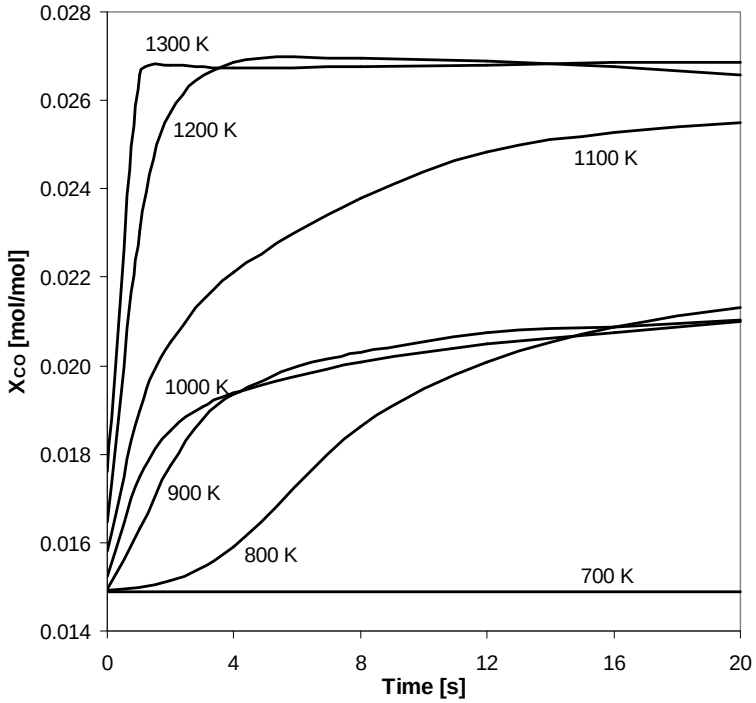

Fig. 2-16. Calculated carbon monoxide mole fractions X_{CO} from natural gas fires at $\Phi = 2.17$ as a function of time for isothermal conditions at the temperatures indicated. Initial conditions from Morehart’s hood experiments (cf. Sect. 2.4.2) (reproduced from Pitts (1995)).

Pitts compared the results of chemical-kinetic calculations with experimental data and concluded that in hood experiments increased temperatures lead to higher fractions of CO_2 but almost unaffected fractions of CO (cf. Sect. 2.4.2), while chemical-kinetic calculations clearly indicate that the formation of CO would be strongly favoured and the amount of CO_2 would be expected to remain nearly constant (Pitts 1994).

2.4.5 Experiments in the ISO 9705 room within the TOXFIRE project

2.4.5.1 Original work

Lönnermark, Blomqvist et al. (Lönnermark et al. 1996, Blomqvist and Lönnermark 2001, Mansson et al. 1996) performed large-scale tests in the ISO 9705 (ISO 1993) room within the TOXFIRE-project (Petersen and Markert 1999). The room (l * w * h = 3.6 m * 2.4 m * 2.4 m), made out of lightweight concrete, was insulated in its upper half by 50 mm high density mineral wool and was equipped with a 0.8 m wide opening vent that was centrally located in one of the shorter walls. To alter the ventilation conditions, at constant soffit height of 2.0 m, different vent heights H were used: 0.89 m, 0.68 m, 0.56 m, and 0.45 m. Five different solid and liquid fuels were burned in pans of different size from 0.5 m^2 to 1.4 m^2. Extensive gas samplings were performed in the opening vent and in the duct of the gas collecting hood (Fig. 2-17), from which species yields were calculated by the related mass flows. For each test one or more periods of quasi-steady states were defined, to correlate the actual GER with species yields. The GER was determined directly with a phi-meter in the opening (cf. Sect. 2.3.3). Soot clogging occurred at the phi-meter, so that for chlorobenzene (CB) the GER was determined by the mass flows calculated from the thermocouple measurements (cf. Sect. 2.3.2).

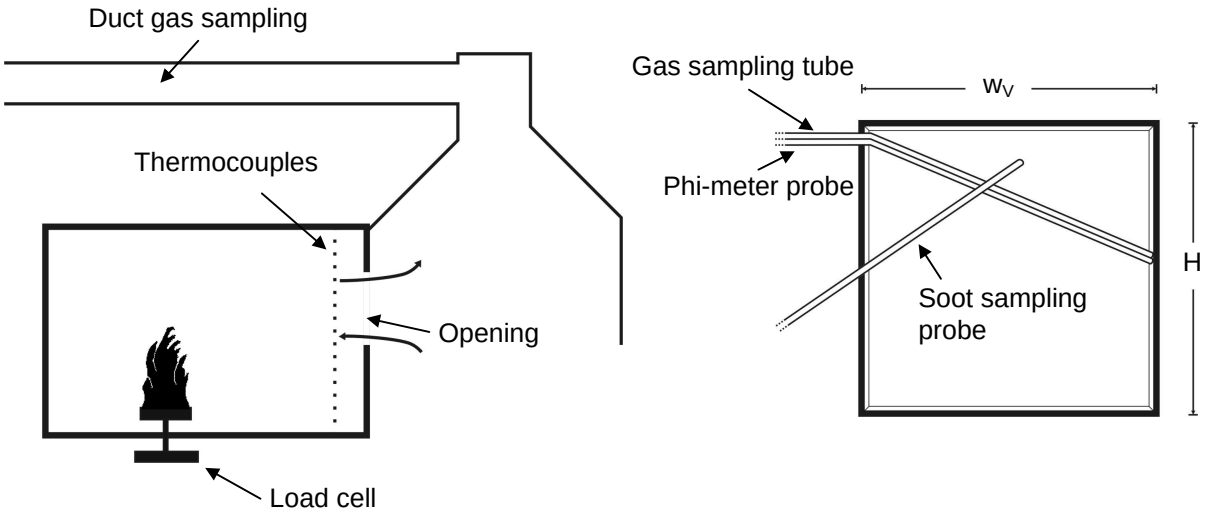

Fig. 2-17a+b. Diagram of the ISO 9705 compartment with exhaust duct (a) and instrumentation in front of the opening (b) (reproduced from Lönnermark and Babrauskas (1996)).

Lönnermark and Babrauskas (1996) compared the air inflows through the compartment vent by recalculation of the phi-meter readings and from the thermocouple data. By means of some examples (Fig. 2-18) they showed that the phi-meter generally predicted higher mass flows, especially for small opening heights. Lönnermark, Blomqvist et al. decided to publish the results of the ISO 9705 room tests with the GER given by the phi-meter readings (when available). In contrast, the species yields measured in the opening vent

were calculated based on mass flows from thermocouple measurements (Lönnermark et al. 1996, Lönnermark 2005a, Blomqvist and Lönnermark 2001, Blomqvist 2005).

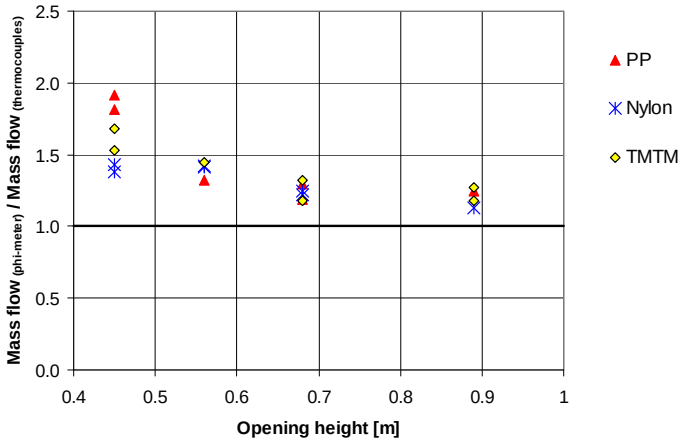

Fig. 2-18. The ratio of the mass flows calculated from phi-meter readings and from the thermocouple data in dependence on the opening height. The values were given by example without reference to an exact test series (reproduced from Lönnermark and Babrauskas (1996)).

Although large-scale tests with self-regulating mass loss rates are difficult to analyse, a fairly comprehensive data set could be achieved for fires of the polymer nylon 66 (Ny) and the crystalline organic compound tetrametylthiuram monosulphide (TMTM). In accordance with Sect. 2.4.3, the results are presented as normalised yields of CO_2 (Fig. 2-19a and Fig. 2-20a) and yields of CO (Fig. 2-19b and Fig. 2-20b). The opening height H and the reported GER for flashover ("fo", defined as the GER when flames come through the opening (Lönnermark et al. 1996, p. 110)) are also mentioned. Opening yields of CO from under-ventilated fires of TMTM were not reported due to interference problems in the FTIR spectra.

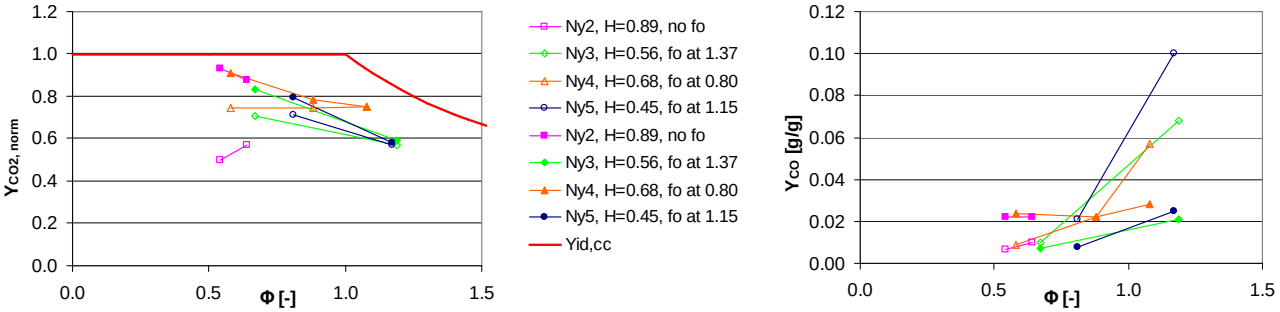

Fig. 2-19a+b. Normalised yields of CO_2 and yields of CO from fires of nylon 66 (Ny) measured in the opening (open dots) and in the exhaust duct (closed dots). Yields are correlated with the reported $\Phi_{phi\text{-}meter}$. Dots from the same test-# are connected (data taken from Lönnermark et al. (1996)).

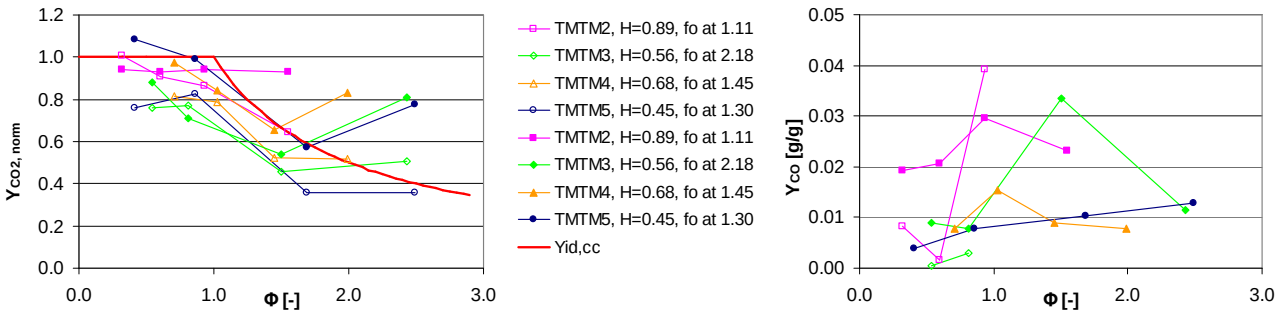

Fig. 2-20a+b. Normalised yields of CO_2 and yields of CO from fires of tetrametylthiuram monosulphide (TMTM) measured in the opening (open dots) and in the exhaust duct (closed dots). Yields are correlated with the reported $\Phi_{phi\text{-}meter}$. CO yields from under-ventilated fires measured in the opening are not reported due to interference problems. Dots from the same test-# are connected (data taken from Lönnermark et al. (1996)).

The general correlations of CO and CO_2 yields measured in the opening with the GER are confirmed by the experiments. It is expected that for well-ventilated fires the species yields measured in the opening equal the yields measured in the duct, because no external combustion takes place. For some tests the CO yields measured in the opening are lower than those measured in the duct (Ny2, Ny4 (partly), TMTM2 (partly), TMTM3). However, an increase of CO between the opening and the duct was ruled out (Blomqvist 2006). For increased GERs, external combustion might occur resulting in increased duct yields of CO_2 while CO decreases on the way from the opening to the duct. The expected behaviour is generally confirmed by the experimental results. When the measurements at the opening and at the duct are compared, the behaviour of the yields of CO (Fig. 2-19b and Fig. 2-20b) and CO_2 from TMTM (Fig. 2-20a) indicates combustion outside the control volume for GERs significantly smaller than the reported GERs of flashover. For Ny the yields of CO_2 do not support the early influence of external combustion. A detailed discussion of the phenomenon of external combustion is not given.

2.4.5.2 Some remarks on the experiments in the ISO 9705 room within the TOXFIRE project

Within this work it was examined whether the air inflows based on temperature measurements or calculated from phi-meter readings are correct. The mass flows were not explicitly reported by Lönnermark et al. (1996). Instead the mass flows based on phi-meter readings were calculated by Equation (2-1) from the given phi-meter readings and mass loss rates. The mass flows from thermocouple data were calculated by Equation (2-14) from reported compartment temperatures T_{comp}. As given by Lönnermark et al. (1996), T_a = 293 K and C_v = 0.68 were used.

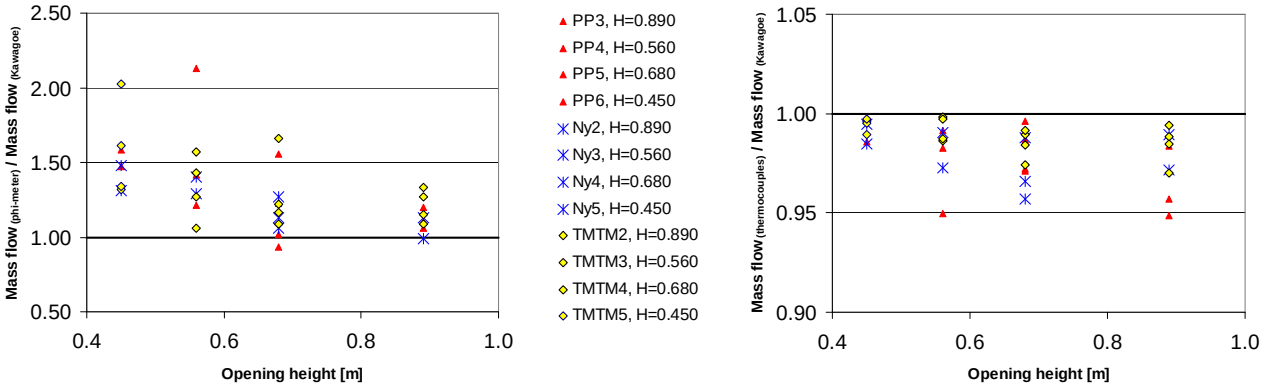

Fig. 2-21a+b. Comparison of normalised mass flows calculated from reported phi-meter values (a) and from reported thermocouple data (b) (note the different scales). The normalisation is done by values from the Kawagoe-Equation (2-15) (calculated from data of Lönnermark et al. (1996)).

Both data sets are normalised by the Kawagoe-Equation (2-15). The results are illustrated in Fig. 2-21a+b. From Fig. 2-21a the trend of Fig. 2-18 is confirmed and it is revealed that the air inflows which are implied in the phi-meter readings are often higher than achievable in compartment fires (cf. Sect. 2.3.6). This is especially the case for small opening heights where the mass flows from phi-meter readings are sometimes double the expected mass flows. The Equation (2-15) was applied with a constant orifice coefficient C_v although a slight dependence of the coefficient was found such that the coefficient decreases with decreasing vent height (Steckler et al. 1984). Taking this effect into account would slightly amplify the trend depicted in Fig. 2-21a.

In contrast, the air inflows from thermocouple data are in close accordance with the results of the Kawagoe-Equation (Fig. 2-21b). The ratio is always between 0.94 and 1.0. The slight trend is a side effect of the temperature dependence on the opening height.

From this comparison it must be concluded that the reported GER, which was represented by the phi-meter readings, has to be amended by the reciprocal factor of the over-estimation of the air inflows. A possible explanation of the deviation of the phi-meter readings is that the gas probes were not exactly mounted in the vent to represent the average mixture of out-flowing gases. This seemed to be the case especially for small opening heights, where the shear layer between inflow and outflow is relatively thick compared to the opening height (cf. Sect. 3.2.1). It is known from species mappings of out-flowing gases that the mixture is not well-stirred but becomes richer with increasing elevation (cf. Sect. 3.3). It must be assumed that the phi-meter probes partly aspirated gas mixture from the shear layer or from a less rich elevation.

Application of the amendment results in new GERs, while the species yields do not need to be corrected, because they were already based on vent flows from thermocouple measurements and independent duct flows respectively (Mansson 1996).

In Fig. 2-22a+b and Fig. 2-23a+b the species yields from the opening (open dots) and from the duct (closed dots) are correlated with the amended equivalence ratios Φ_{temp} from temperature measurements. The vent height H and the amended GER of flashover are also given. The normalised CO_2 yields measured in the opening (Fig. 2-22a and Fig. 2-23a) are generally closer to the ideal curve than before. CO_2 yields from duct measurements that exceed the ideal curve are an indication of external combustion. Regarding the CO yields at the opening plane, the area where the yields increase compared to yields from well-ventilated fires is shifted to a GER by about 1. The new results are in qualitative agreement with the results from Gottuk and Lattimer's methodology for upper layer temperatures exceeding 900 K (Eq. (2-20b)). In the Toxfire experiments, with the exception of PP6 (837 K), the upper layer temperatures varied between 905 K and 1270 K at GER ≈ 1. The quantitative comparison shows that the CO yields at the opening plane are frequently lower than predicted by Equation (2-20b). As the opening yields were also frequently lower than the duct yields, it must be suspected that the CO yields from opening plane measurements were too low. A possible explanation would be similar to that for the deviation of the phi-meter readings, because the phi-meter probes and the gas probes were mounted next to each other (Fig. 2-17b). When the probes predominantly aspirated gas from lower elevations of the outflow, the concentration of CO_2 is over-represented compared to the CO concentration (cf. Sect. 3.3).

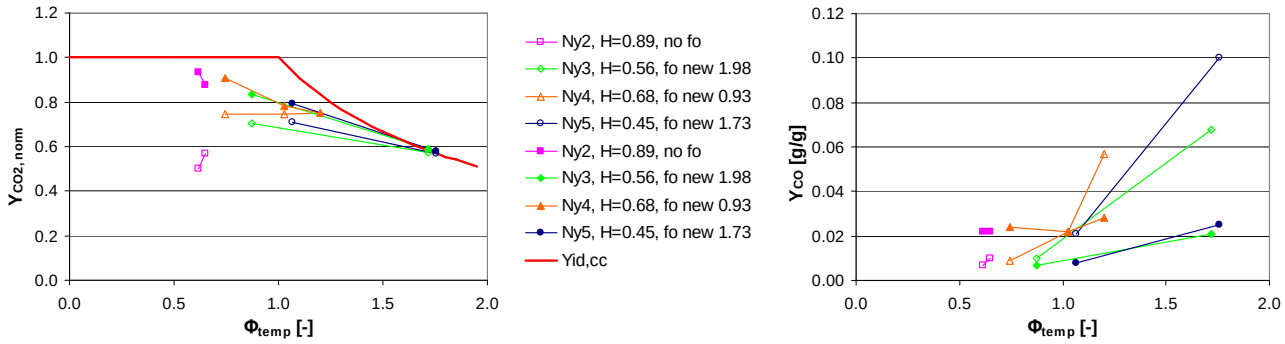

Fig. 2-22a+b. Normalised yields of CO_2 and yields of CO from fires of nylon 66 (Ny) measured in the opening (open dots) and in the exhaust duct (closed dots). Yields are correlated with the amended Φ_{temp} (calculated from data of Lönnermark et al. (1996)).

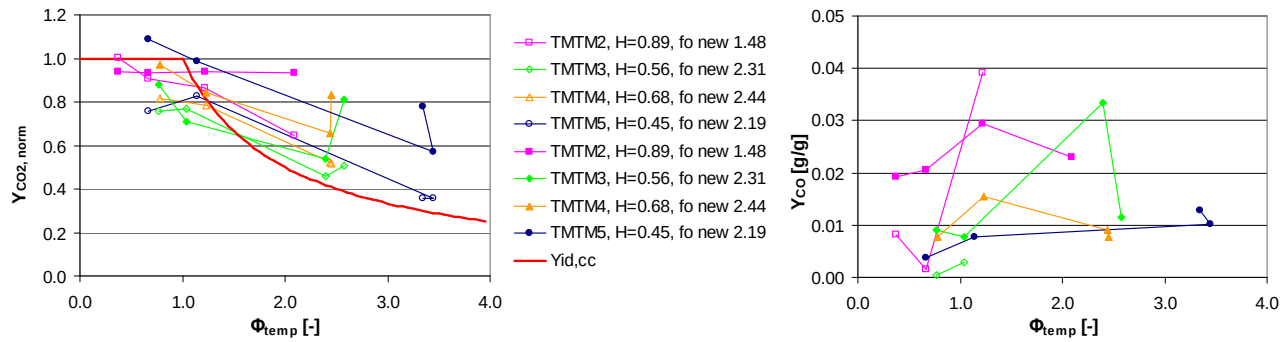

Fig. 2-23a+b. Normalised yields of CO_2 and yields of CO from fires of tetrametylthiuram monosulphide (TMTM) measured in the opening (open dots) and in the exhaust duct (closed dots). Yields are correlated with the amended Φ_{temp} (calculated from data of Lönnermark et al. (1996)).

2.4.6 The iBMB research

2.4.6.1 Original work

Hosser et al. (2000) conducted under-ventilated fire tests in a controlled ventilation cone calorimeter and the ISO 9705 compartment. One aim of the research work was the investigation of the correlation of CO yields with the GER in different scales. The fuels studied were polyethylene granules (PE), ethylene glycol (glycol) and for the larger scale studies spruce in addition. For the evaluation, all measurements were time-averaged so that only one data set was derived from each test. The averaging interval was between 10 % and 90 % mass loss for the cone calorimeter and between 10 % and 80 % mass loss for the ISO 9705 room based on the total mass loss.

Will (2005) recently presented an extensive discussion of the results with the controlled ventilation cone calorimeter. The calorimeter (Fig. 2-24) was a modification developed by the iBMB based on the standard cone calorimeter according ISO 5660 (ISO 1999, Babrauskas 2002). The compartment volume was 0.13 m^3 with exhaust gas probes mounted in the exhaust duct. This design was chosen to prevent external combustion from influencing the results. CO_2, CO and O_2 measurements were performed following the ISO 5660 standard. Additionally, a second CO_2/CO analyser with extended measurement range was used to account for the increased gas concentrations from the closed system. The air inflow was controlled by a mass flow controller.

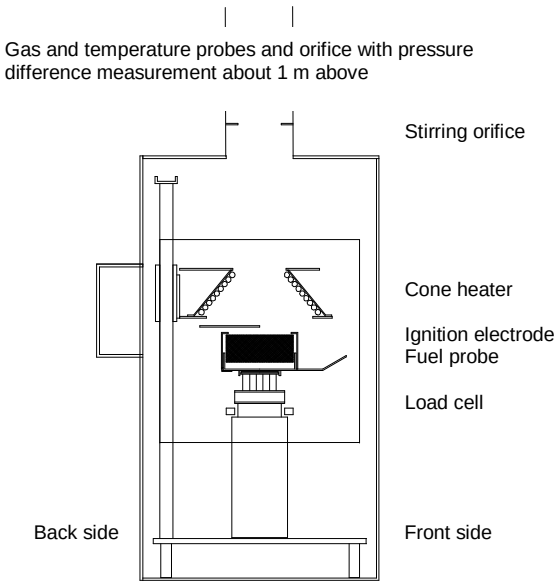

Fig. 2-24. The iBMB controlled ventilation cone calorimeter (taken from Will (2005)).

Fuel samples of PE and glycol were exposed to 15, 25, and 40 kW/m^2 radiation by the cone heater and ignited by the ignition electrode. The mass loss rate per unit area was shown to increase with increased radiation intensity. A dependence on the ventilation

conditions was also given such that with the GER exceeding about 0.5, the mass loss rate per unit area decreased (Will 2005, p. B-65).

Normalised yields of CO_2 and yields of CO from PE and glycol from tests with three levels of radiation are given in Fig. 2-25 and Fig. 2-26. For both fuels the CO_2 yields exhibit a generation efficiency of about 0.8 of the ideal yield that is virtually independent of the radiation intensity. CO yields are generally higher from PE than from oxygen-containing glycol. For over-ventilated conditions the CO yields decrease with increased radiation intensity. This is a side effect from increased temperatures and is consistent with the behaviour expected from chemical kinetics.

For under-ventilated conditions less data exists and the behaviour with respect to the radiation intensity is less clear. However, it can be seen that the fuel structure is of less importance for under-ventilated conditions: The factor of about 25 between the average CO yields from PE ($Y_{CO} \approx 0.02$ g/g) and glycol ($Y_{CO} \approx 0.0008$ g/g) for well-ventilated conditions decreased significantly for under-ventilated conditions. Beyler (1986a) stated that under fuel-rich conditions the ratio is reversed and oxygenated hydrocarbons generate

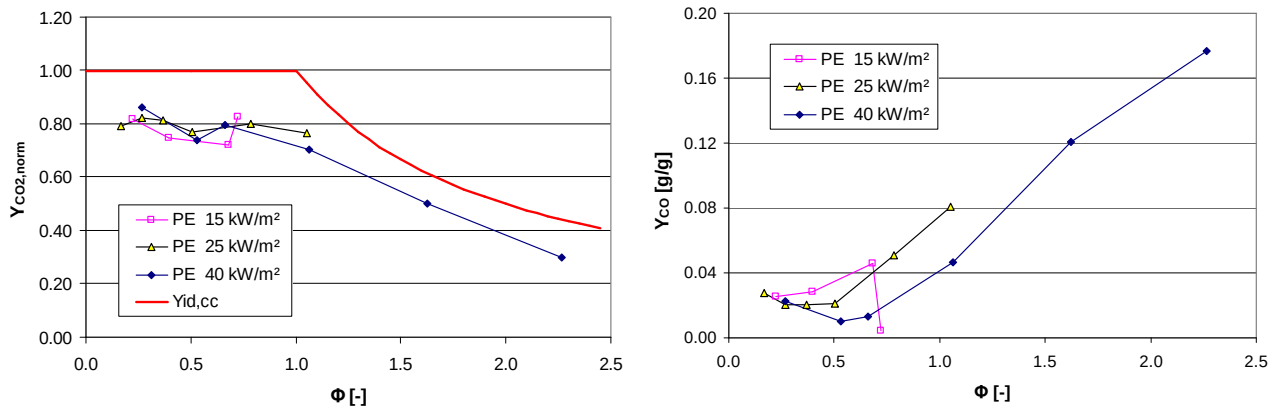

Fig. 2-25a+b. Normalised yields of CO_2 and yields of CO from PE fires in the cone calorimeter. Data of equal radiation intensities is connected (data taken from Will (2005)).

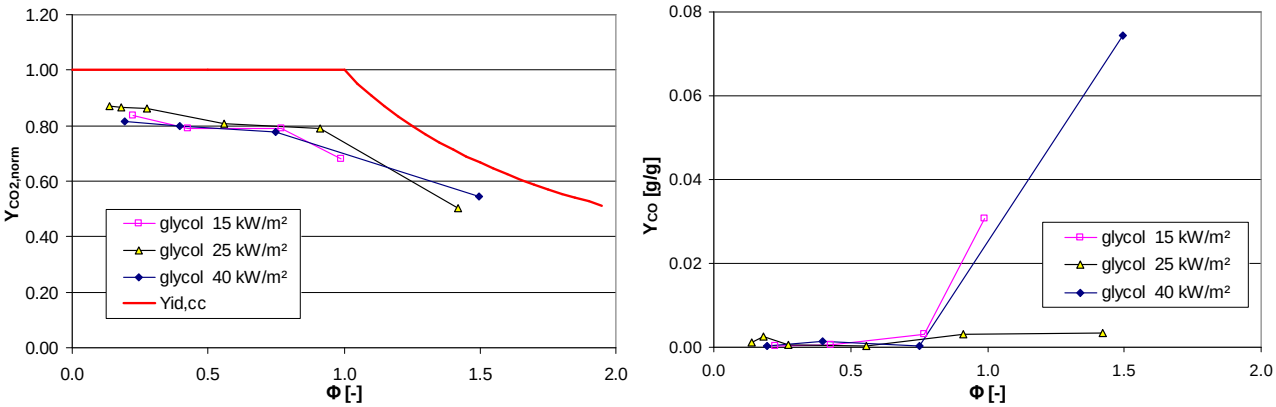

Fig. 2-26a+b. Normalised yields of CO_2 and yields of CO from glycol fires in the cone calorimeter. Data of equal radiation intensities is connected (data taken from Will (2005)).

higher normalised yields of CO than pure hydrocarbons. This is not confirmed by the iBMB experiments. Ignoring one outlying data point (PE, 40 kW/m^2), in both experiments the increase of the CO yields compared to well-ventilated conditions starts at about $\Phi = 0.7$. For glycol at 25 kW/m^2 this happens on a smaller level. Temperatures inside the cone calorimeter chamber were not measured.

The design of the ISO 9705 room corner test facility (ISO 1993) of the iBMB was similar to the compartment of Lönnermark et. al. (Sect. 2.4.5). However, the compartment of lightweight concrete was used without wall and ceiling insulation and the width of the door vent was altered. At a constant vent height of 2.0 m the width was altered between 0.04 m and 0.80 m. Gas sampling was performed only in the exhaust duct. The gas analysis was carried out as described before for the standard cone calorimeter. The smoke obscuration was also measured online as specific extinction area, SEA, that is related to the burned fuel mass (Foley and Drysdale 1994). The mass flows through the opening vent were measured by bi-directional probes as described in Sect. 2.3.4. For the tests with three different fuels, PE (25 kg, 0.5 m^2 pool), glycol (22.5 kg, 1.0 m^2 pool) and spruce (35 kg, crib), the initial fuel weight and the pool area or crib size respectively was kept the same. Only the opening width w_V was altered at each test. The results are presented in Table 2-1. Normalised yields of CO_2 and the CO yields are additionally displayed in Fig. 2-27.

Table 2-1. Results of the iBMB tests in the ISO 9705 compartment. All time-dependent parameters are reported as average values (data taken from Hosser et al. (2000) with exception of the last column).

Test -#	Fuel	w_v [m]	Φ_{rep} [-]	$\dot{m}_f$ [kg/s]	$\dot{m}_{air}$ [kg/s]	Y_{CO2} [kg/kg]	Y_{CO} [kg/kg]	SEA [m^2/kg]	Φ_{J-T} [-]
17	PE	0.8	0.24	0.012	0.724	2.240	0.017	398.997	*0.19*
15	PE	0.4	0.52	0.012	0.332	2.084	0.023	372.853	*0.35*
16	PE	0.2	0.96	0.011	0.164	2.094	0.050	358.513	*0.62*
18	glycol	0.4	0.33	0.018	0.307	1.028	0.000	0.000	*0.25*
19	glycol	0.2	0.83	0.023	0.151	1.031	0.001	0.364	*0.55*
20	glycol	0.1	1.68	0.021	0.068	0.898	0.023	0.079	*0.94*
25	glycol	0.04	3.03	0.015	0.027	0.845	0.073	1.164	*1.68*
8	spruce	0.8	0.33	0.041	0.634	1.076	0.002	4.867	*0.25*
9	spruce	0.2	1.22	0.034	0.144	1.138	0.004	6.085	*0.72*
10	spruce	0.1	2.20	0.030	0.071	0.966	0.028	16.176	*1.26*
12	spruce	0.04	7.25	0.025	0.018	0.563	0.142	81.173	*2.66*

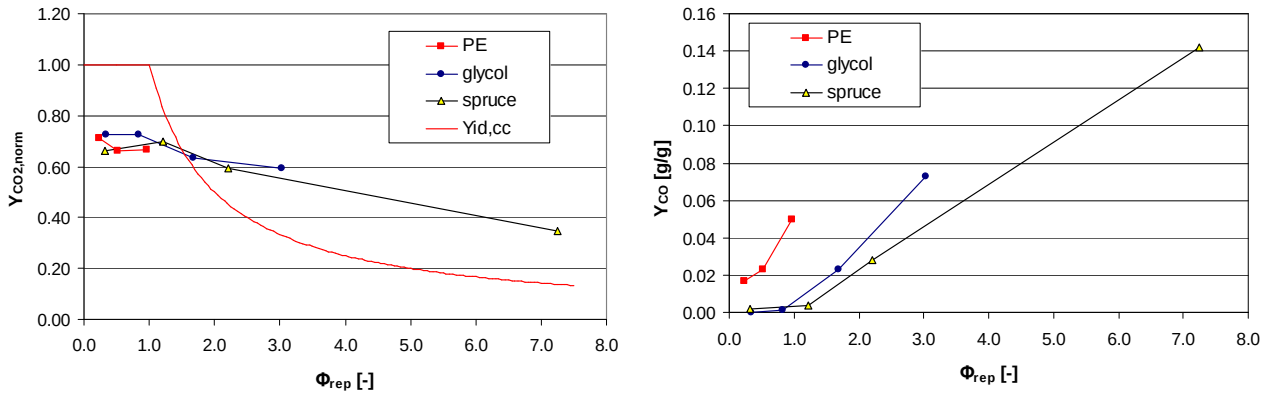

Fig. 2-27a+b. Normalised yields of CO_2 (a) and yields of CO (b) from fires in the iBMB ISO 9705 compartment. Yields are correlated with the reported GER (data taken from Hosser et al. (2000)).

2.4.6.2 Some remarks on the experiments in the ISO 9705 room within the iBMB project

From Fig. 2-27a, the generation efficiency of CO_2 for over-ventilated fires is between $Y_{CO2,norm} = 0.70$ and $Y_{CO2,norm} = 0.75$. In contradiction, for under-ventilated conditions the efficiency from the glycol fire #25 ($\Phi_{rep} = 3.03$) is 1.8 times higher than expected from ideal combustion. For the spruce fire #12 ($\Phi_{rep} = 7.25$) this factor is 2.5. In addition these factors are to be divided by the real generation efficiency.

One explanation for this behaviour is a considerable CO_2 generation by external combustion, where more CO_2 was generated outside than inside the compartment. This is not reported. In fact external combustion is only mentioned for PE fires (Blume 2003, p. 89). Another explanation could be the compartment's dead storage volume, which plays a role because the test fires only represent quasi-steady state conditions. The gross volume of the ISO 9705 compartment contains about 5.7 kg of oxygen that represents about 1.8 kg of typical hydrocarbon fuel to be burned without extra oxygen. Since the initial fuel mass was always more than 10 times this mass, and the averaging interval started after 10 % of the total mass loss was reached, any significant influence of the dead storage volume must be discounted.

The raw data sets from the iBMB ISO 9705 compartment fires contain temperature measurements from a front corner thermocouple tree and a thermocouple tree within the opening vent. The data provides the opportunity for an alternative calculation of the mass flows according the method of Jansson and Tran (cf. Sect. 2.3.1). This data is compared with the original mass flows calculated from the vent thermocouple tree and bi-directional pressure probes (cf. Sect. 2.3.4). An orifice coefficient of 0.68 was used for both methods (cf. (Blume 2002, p. 86)). From the examples of test fires #12 and #16, the air inflows according to both methods are compared (Fig. 2-28a+b). Both results exhibit the similar trend, with the new method generally predicting higher mass flows. The Kawagoe-

Equation (2-15) yields 0.0588 kg/s for fire #12 and 0.294 kg/s for fire #16 as indicated in the figure. The discrepancy with the Kawagoe-Equation might be partly due to the low upper layer temperatures of 588 K and 833 K respectively, averaged 0.30 m under the ceiling for both fires. A comparison of time-averaged mass flows from all tests listed in Table 2-1 is given in Fig. 2-29, where the trend from the time-dependent illustrations is confirmed.

The application of bi-directional pressure probes relies on the assumption that the probes capture the maximum flow velocity, from which the average flow is calculated by the orifice factor (Sect. 2.3.4). If the probes are not adjusted correctly to the flow direction, or if their location does not represent the location where the maximum flow velocity occurs, the result will be an under-estimation (Babrauskas 1984, Emmons 2002). However, even after intensive discussion with the researchers involved, the reasons for the deviations of the mass flows could not be fully assigned.

The mass flows from Jansson and Tran's method lie in between the results from different approaches and are also backed up by the general literature. After all the method is based on temperature measurements as already done for the amendments from the TOXFIRE ISO 9705 room fire tests (Sect. 2.4.5.2). Therefore the newly calculated mass flows are believed to be more reliable. A comparison of the air inflows achieved from both European test series with the ISO 9705 compartment is given in Fig. 2-30. The amended inflows calculated for the TOXFIRE compartment are lower than the original data. They are still slightly higher than the amended inflows calculated for the iBMB compartment, which are increased compared to the original data.

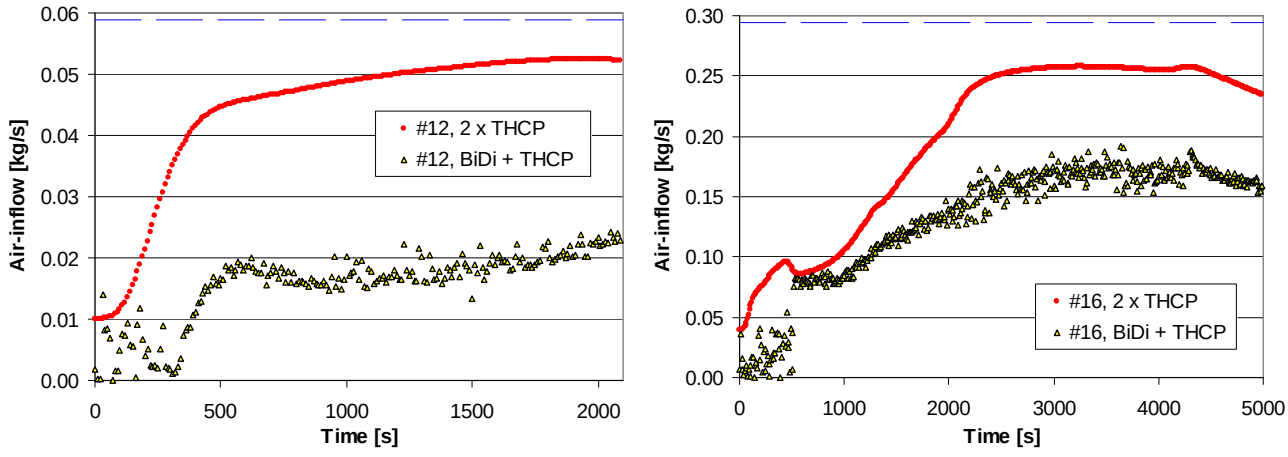

Fig. 2-28a+b. Comparison of two time-dependent methodologies to obtain air inflows by example of the iBMB test fire #12 (a) and #16 (b). The expected results from Equation (2-15) are also given.

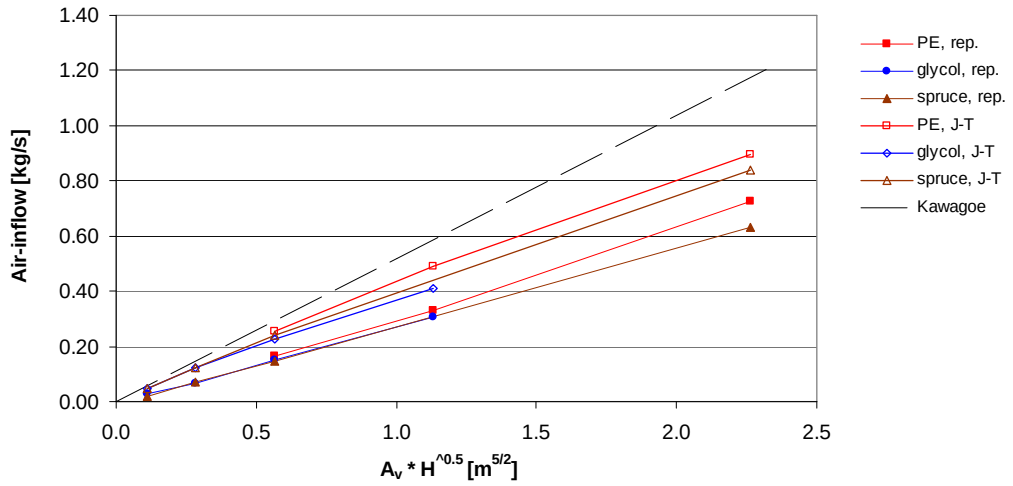

Fig. 2-29. Comparison of the time-averaged air inflows reported from original calculation (closed dots), calculated by the method of Janssen and Tran (open dots), and expected from Equation (2-15).

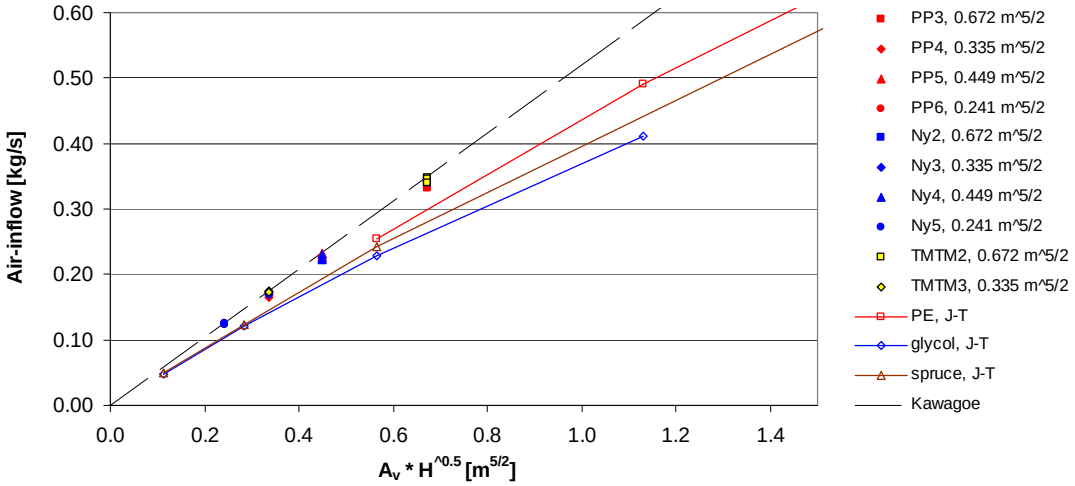

Fig. 2-30. Newly calculated air inflows from the TOXFIRE test series (closed dots) and the iBMB test series (open dots, connected) with the ISO 9705 compartment. As tests with the same ventilation factor achieved very similar mass flows, some dots are hidden. Comparison by Equation (2-15).

From the new mass flows an amended GER $\Phi_{J\text{-}T}$ is calculated as listed in the last column of Table 2-1. When the species yields are correlated with the amended GER (Fig. 2-31a), unexplainable high generation efficiencies of CO_2 do not occur (cf. Fig. 2-27a). The increase of the CO yields starts at over-ventilated conditions for all fuels (Fig. 2-31b). This is consistent with previous findings from hood experiments. The highest GER achieved in spruce fires decreased from $\Phi_{rep} = 7.25$ to $\Phi_{J\text{-}T} = 2.66$. This value is in much better accordance with previous results from compartment fires with centrally located, un-dispersed wood cribs (Drysdale 1998, p. 332).

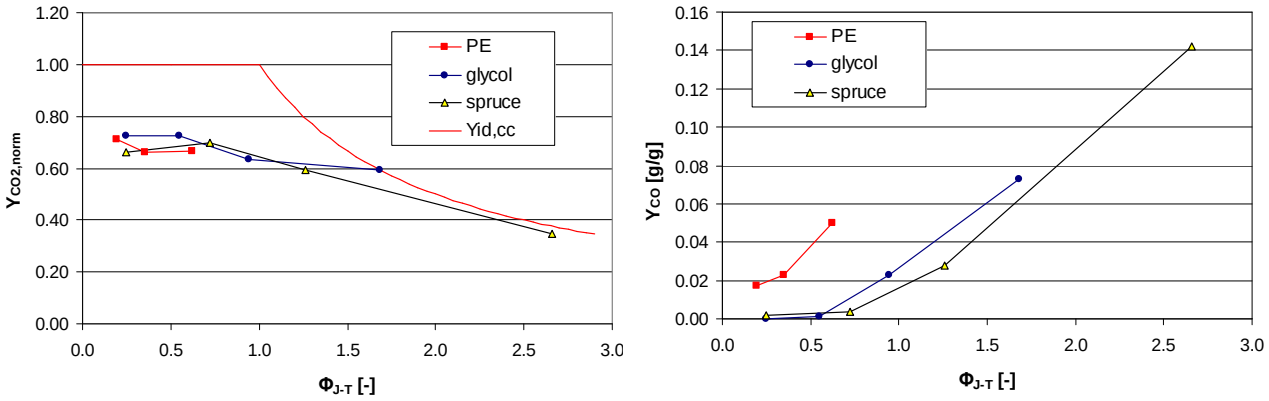

Fig. 2-31a+b. Normalised yields of CO_2 (a) and yields of CO (b) from fires in the iBMB ISO 9705 compartment. Yields are correlated with the amended GER.

2.4.7 Wieczorek's methodology

2.4.7.1 Original work

A recent study on carbon monoxide generation and transport from compartment fires correlated with the GER was performed by Wieczorek (2003) also at the Virginia Polytechnic Institute and State University. For his "compartment study", he used an insulated half-scale ISO 9705 compartment (1.17 m * 1.78 m * 1.17 m high) with a door-like opening centrally located in one of the shorter walls. This 0.82 m high door was varied in its width from 0.076 m, 0.165 m, 0.330 m to 0.660 m. To achieve steady state conditions, he used a 0.305 m diameter propane burner that was supplied by an LPG tank capable of reaching stable pre-set heat release rates of between 50 kW and 500 kW. Species (O_2, CO_2, CO, and THC) sampling was done in the doorway by a gas rake that covered the complete outflow area. Mass flows through the compartment vent were calculated by an array of bi-directional probes (cf. Section 2.3.5). In his evaluation Wieczorek left out the results of the smallest opening width (0.076 m). He reported that because the area of the doorway (0.06 m^2) was smaller than the area of the gas burner (0.07 m^2), the scenario "represented a jet diffusion flame (at the opening) as opposed to a typical compartment fire" (Wieczorek 2003, p. 149). The CO yields correlated with the GER (Fig. 2-32) indicate a strong dependence on the opening width, i. e. with increasing opening widths much higher yields are generated. Wieczorek concluded that "the GER concept is not appropriate for correlating and predicting species generation in prototypical building fires" (Wieczorek et al. 2004b), as external combustion especially by flame extensions has to be taken into account. Wieczorek developed a methodology that reflects the proportion of flaming combustion within the doorway: he proposed a non-dimensional heat release rate $\widetilde{Q}$ defined as the ideal HRR $\dot{Q}_{id}$ divided by the HRR required for the

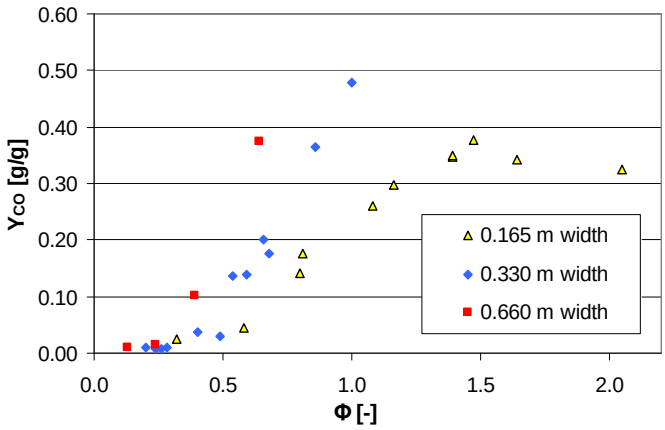

Fig. 2-32. Yields of CO correlated with the GER from propane fires in an half-scale ISO 9705 compartment. Data from opening widths of w_V = 0.165 m, 0.330 m, and 0.660 m (data taken from Wieczorek (2003)).

flame to reach the compartment doorway $\dot{Q}_{FlameExtensions}$

$$\widetilde{Q} = \frac{\dot{Q}_{id}}{\dot{Q}_{FlameExtensions}} \tag{2-21}$$

where

$$\dot{Q}_{id} = \dot{m}_f * \Delta H_C \tag{2-22}$$

Wieczorek defined four regions for $\widetilde{Q}$ illustrated in Fig. 2-33:

$$\widetilde{Q} = \begin{cases} < 1 & - \text{ Combustion within the compartment} \\ = 1 & - \text{ Flame tip at the compartment doorway} \\ > 1 & - \text{ External burning due to flame extensions} \\ \geq \widetilde{Q}_{crit} = \dfrac{\dot{Q}_{Ventilation-limit}}{\dot{Q}_{FlameExtensions}} & - \text{ External burning due to under-ventilated conditions} \end{cases}$$

where

$$\dot{Q}_{Ventilation-limit} = \dot{Q}_{id}(\phi = 1) \tag{2-23}$$

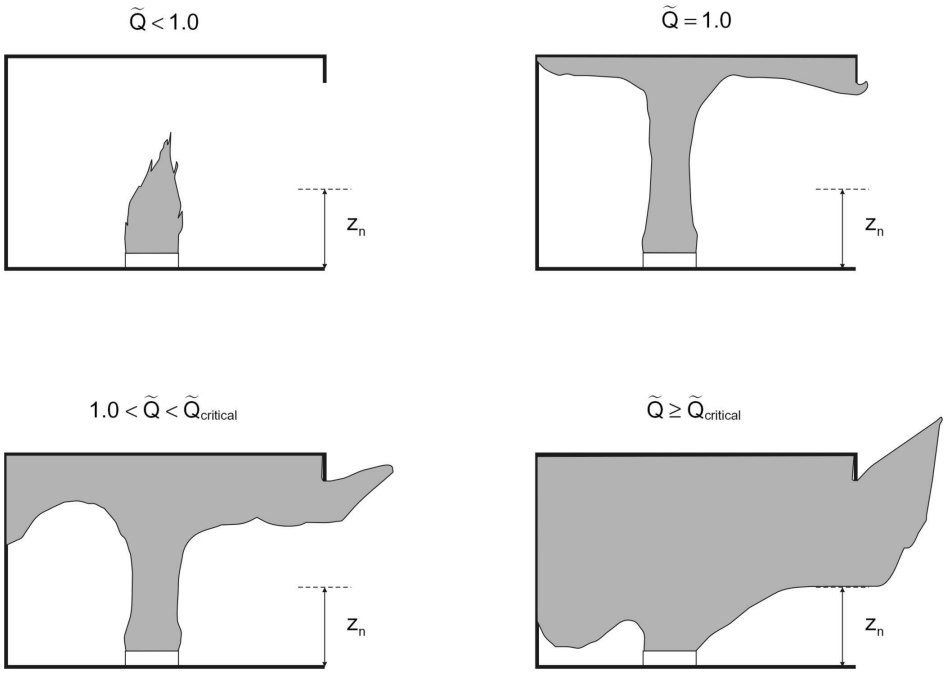

Fig. 2-33a-d. Illustration of four conditions for $\widetilde{Q}$ with neutral plane height z_n (reproduced from Wieczorek (2003)).

To calculate the species yields according to his methodology, Wieczorek related the mass flow of generated species $\dot{m}_i$ to the fuel combustion rate within the compartment $\dot{m}_{f,comp}$ instead of relating it to the complete fuel mass flow $\dot{m}_f$. By applying this methodology, the reported species yields correlated with the parameter $\widetilde{Q}$ collapsed to a single curve for all three considered ventilation conditions (Fig. 2-34). The methodology was not applied to any other compartment fire data set.

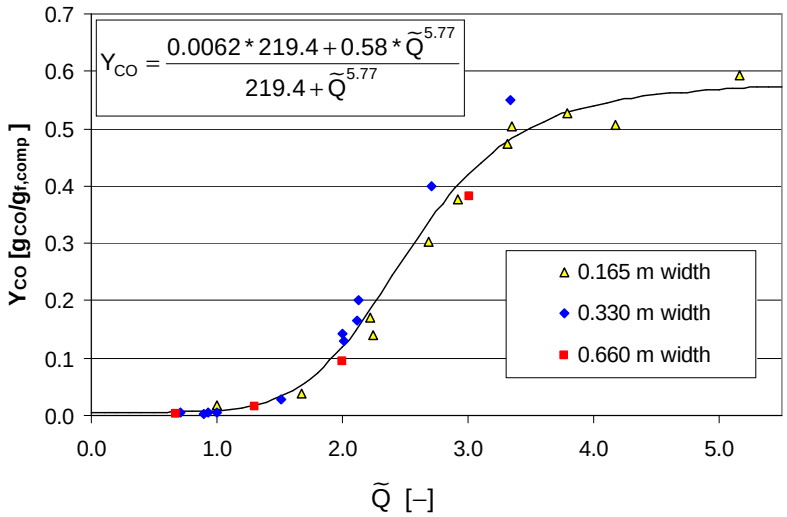

Fig. 2-34. Yields of CO correlated with $\widetilde{Q}$ from propane fires in a half-scale ISO 9705 compartment (taken from Wieczorek (2003, p. 99) and Wieczorek et al. (2004b)).

In his “hallway study” Wieczorek (2003) also studied the species development and transport through a 6.1 m long hallway that was attached to the original compartment. With the 0.330 m wide compartment-to-hallway vent he tested three (again w_V = 0.165 m,

0.330 m, and 0.660 m) hallway-to-ambient air opening widths and produced over-ventilated steady state fires with a heat release rate of 85 kW, 127 kW, and 150 kW. He showed that the species composition at the compartment-to-hallway interface was not affected by the attached hallway and the hallway ventilation condition. On the way through the hallway to the hallway-to-ambient interface the species composition is altered by dilution and, in the case of flame extensions, also by oxidation.

2.4.7.2 Some remarks on Wieczorek's study

In his "compartment study", species yields were measured at the opening vent by a sampling rake that covered the entire outflow plane. From the three data sets he included in his evaluation, flame extensions started with the smallest vent (w_v = 0.165 m) at Φ = 0.51 and with the widest vent (w_v = 0.660 m) at about Φ = 0.26 (Wieczorek 2003, p. 59). By definition the parameter $\widetilde{Q}$ is 1.0 when flame extension starts (Eq. (2-21)). As can be seen from Fig. 2-34, the CO yields are close to zero for $\widetilde{Q} < 1$. For $\widetilde{Q} > 1$, with increasing $\widetilde{Q}$, sampling was done increasingly in the flames, where CO concentrations are elevated (Smith and Cox 1992, Beyler 1986c). Hence, Wieczorek's methodology describes the degree of combustion within the exit plane. It is not suited to predict final species yields that are necessary for risk assessment.

In his "hallway study", Wieczorek reached steady state conditions with the 0.330 m wide compartment vent for different heat release rates (85 kW, 127 kW, and 150 kW). He presented mass flows through the compartment-to-hallway vent and hallway-to-ambient vent. Additionally, area-averaged species concentrations from both vent locations are reported. Unfortunately steady states could be reached only with over-ventilated compartments. Although the data is affected by uncertainties, because species measurements at both locations had to be performed consecutively, the presented data offers the opportunity to calculate species yields and equivalence ratios for both control volumes. In Fig. 2-35 the results are illustrated in comparison with the temperature-dependent Equations (2-20a+b) presented by Gottuk and Lattimer. When the yields from the compartment-to-hallway vent (open dots) are compared with the final yields from the hallway-to-ambient vent (closed dots) at the same GER_{comp}, for small and medium vent widths a significant decrease is shown. The decrease indicates external combustion by flame extensions. For the hallway-ambient vent of w_V = 0.660 m, the results are indistinct, since the measured mole fractions at both locations were very low.

Within the methodology of Gottuk and Lattimer (Sect. 2.4.3) only external burning from under-ventilated conditions is taken into account. Since in Wieczorek's study flame extensions occurred and secondly the extended flames reached into the vitiated upper

layer, the compartment should be used as a control volume. Therefore Φ_{comp} is introduced in Equation (2-20b), as the compartment temperatures are assumed to have exceeded T_{ul} = 900 K (see also (Floyd et al. 2001) and Sect. 4.2). This equation seems reasonably suited to predict CO yields for well-ventilated fires, but one data point at Φ_{comp} = 0.88 exceeds the predicted result (Fig. 2-35). However, the calculated data set of final yields is quite small for a definitive comparison.

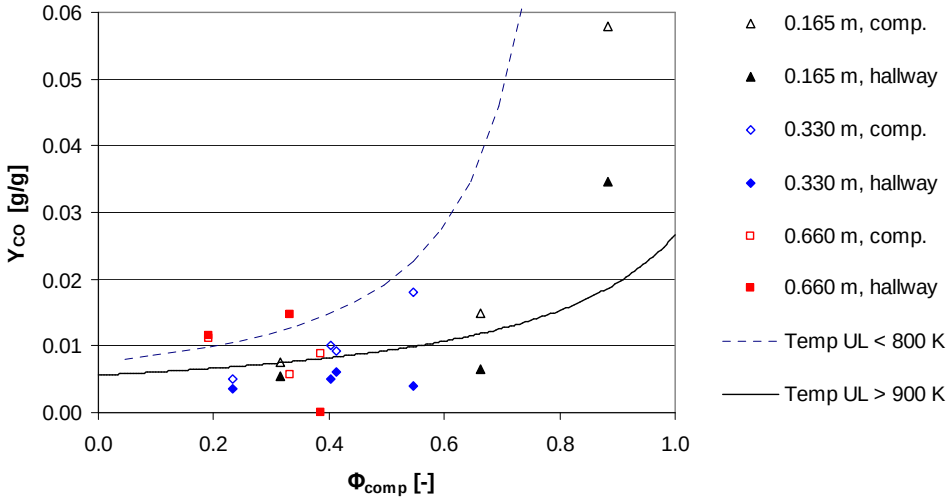

Fig. 2-35. Yields of CO at the compartment-hallway interface (open dots) and at the hallway-ambient interface (closed dots) at three different hallway-ambient vent widths. Comparison with Eqs. (2-20a+b) for two upper layer temperature levels (calculated from data of Wieczorek (2003)).

2.4.8 Conclusions and open questions

Although the global equivalence ratio concept has been subjected to international research for more than twenty years, there is still no consensus regarding understanding of the main phenomena. The present situation was recently summarised by Pitts (2006): “It is clear to me that the formation of CO in enclosures is much more complicated than I had originally hoped when I proposed the use of the GER concept based on the results of hood experiments. There seems to be lots of room for research and innovative ideas.” The essential points concerning the basic data are discussed below.

2.4.8.1 Determination of the global equivalence ratio

The accuracy of the determination of the GER depends on the measurement accuracy of the fuel mass flow $\dot{m}_f$ and the air mass flow $\dot{m}_{air}$. When experiments were performed with gaseous fuel with preset fuel supply rate, a very reasonable accuracy of $\dot{m}_f$ must be assumed. For liquid pool fires and fires with solid fuels, the mass loss rate is measured by load cells. Typically steady states cannot be achieved for these kinds of fires, therefore the

mass loss rate was taken from quasi-steady state intervals (cf. Sect. 2.4.6) or by averaging between 10 % and 80 % of the total mass loss (cf. Sect. 2.4.5).

The air mass flows in hood experiments (Sect. 2.4.1 and 2.4.2) were calculated from controlled exhaust gas flow rates. This methodology cannot be scrutinised with hindsight, but is believed to provide reasonably correct results. In the prototype compartment of Gottuk and Lattimer (Sect. 2.4.3), inflow and outflow were separated and the inflow through the inlet duct was assumed to be quite stable and easy to determine.

For freely ventilated compartment fires, the determination of the mass flows is generally more difficult. From the TOXFIRE (Sect. 2.4.5) and the iBMB (Sect. 2.4.6) research studies, which were performed in similar ISO 9705 compartments, the mass flow data originally reported varied considerably (Fig. 2-36). Based on justified considerations, the mass flows and consequently the equivalence ratios were amended.

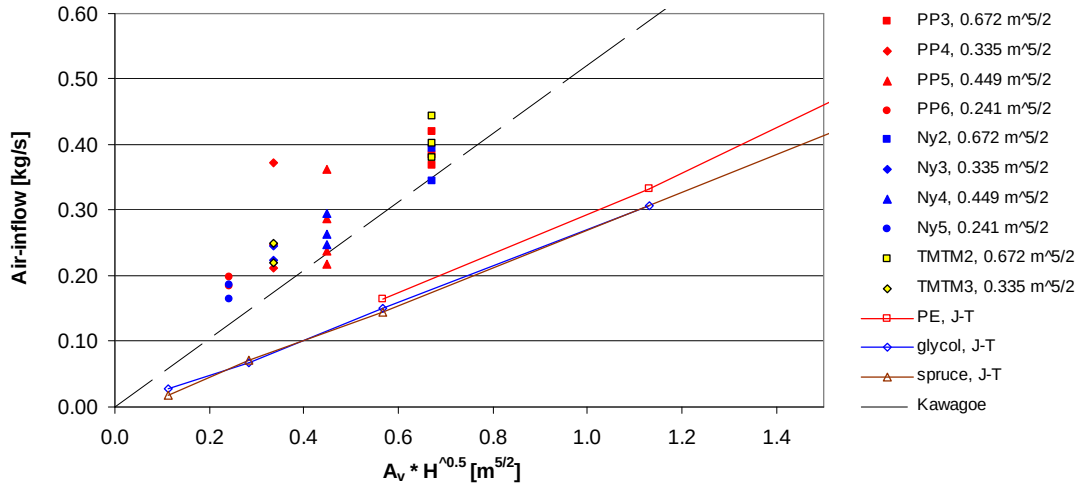

Fig. 2-36. Originally reported air inflows from the TOXFIRE test series (closed dots) and the iBMB test series (open dots, connected) with the ISO 9705 compartment. Comparison by Eq. (2-15).

In Wieczorek's "hallway study", where final species concentrations are reported, the mass flows and species concentrations could only be sampled consecutively. Although long term tests with constant fuel supply rates were performed, Wieczorek reported that steady state conditions could not be fully achieved. A possible error cannot be assigned with hindsight.

2.4.8.2 The correlation of the CO yields with the GER

It is a common observation in all experimental works, that the yields of carbon monoxide increase with increasing GER. With well-ventilated conditions, a basic level $Y_{CO,wv}$ is shown that is independent of the GER. For the equivalence ratio when the CO yield leaves the basic level, a temperature dependence is described: hood experiments indicate a quite distinct transition point between $0.5 < \Phi < 0.6$, where the CO yields start to lift off from the

basic level (cf. Fig. 2-4c, Fig. 2-5a, and Fig. 2-6a). This range was shown to be independent of the burner size and the hood temperature for temperatures between 550 K < T_{ul} < 850 K. In terms of CO yields, the quantitative results were also in reasonable agreement for a wide range of equivalence ratios with hoods of different sizes (cf. Fig. 2-4c and Fig. 2-6a).

From experiments with typical hydrocarbon and oxygenated hydrocarbon fuels, Gottuk and Lattimer presented two equations (Eq. (2-20a+b)) for two temperature regions. The Equation (2-20a), which represents the low temperature level of T_{ul} < 800 K, is derived from Beyler's hood experiments. Equation (2-20b) stands for reactive upper layers of T_{ul} > 900 K. The temperature dependence described by Gottuk and Lattimer does not contradict Zukoski's hood results, since the temperature levels studied by Zukoski et al. represented unreactive upper layers in the sense of Gottuk and Lattimer. The level between 800 K < T_{ul} < 900 K is undefined at Gottuk and Lattimer.

Pitts (Sect. 2.4.4) proposed similar (T_{ul} < 700 K and T_{ul} > 900 K) temperature regions for unreactive and reactive upper layers. However, in his algorithm (Fig. 2-15) $Y_{CO,wv}$ is generally assumed for Φ < 1.0. This late lift-off apparently reflects the square root of 2.8 error of the compartment fire experiments, which lead to an over-estimation of the GER. Hence this contradiction of previous results can be explained.

The ISO 9705 compartment is the largest test facility from which systematic data is available. In Fig. 2-37 the CO yields resulting from the TOXFIRE (Sect. 2.4.5) and iBMB (Sect. 2.4.6) large-scale studies are compiled together. Some remarks concerning the data selected need to be made. From the TOXFIRE experiments the yields from opening samplings are taken when possible, to rule out external combustion. The opening yields are available for Ny and CB. For PP, the duct yields are presented, because they were mostly higher than the opening yields. For TMTM, duct yields are illustrated, since no opening yields are available for under-ventilated fires. A considerable decrease of the duct yields due to external combustion, especially at Φ > 1.5, must be considered for TMTM. From the iBMB tests only duct yields are available. For PE, external combustion was reported without exact reference to the test. It might have occurred as flame extensions, which first occur at the widest opening width (test #17). In this test $\Phi_{J\text{-}T}$ was only 0.19. In the insulated TOXFIRE compartment, generally higher upper layer temperatures were achieved than in the iBMB compartment. The upper layer temperatures are illustrated in Fig. 2-38.

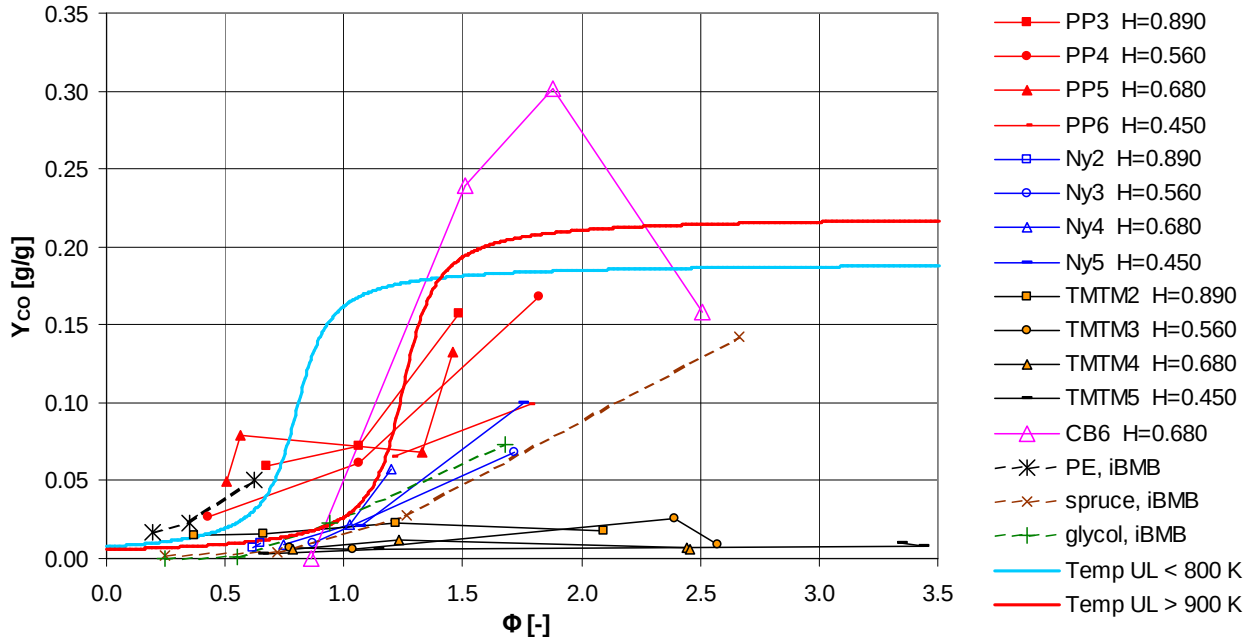

Fig. 2-37. CO yield correlated with the amended GER. ISO 9705 compartment data compiled together from the TOXFIRE test series (open dots: opening yields, closed dots: duct yields, data from one test fire is connected) and iBMB test series (data from different test fires with the same fuel is connected by a dotted line). Comparison with Equations (2-20a+b).

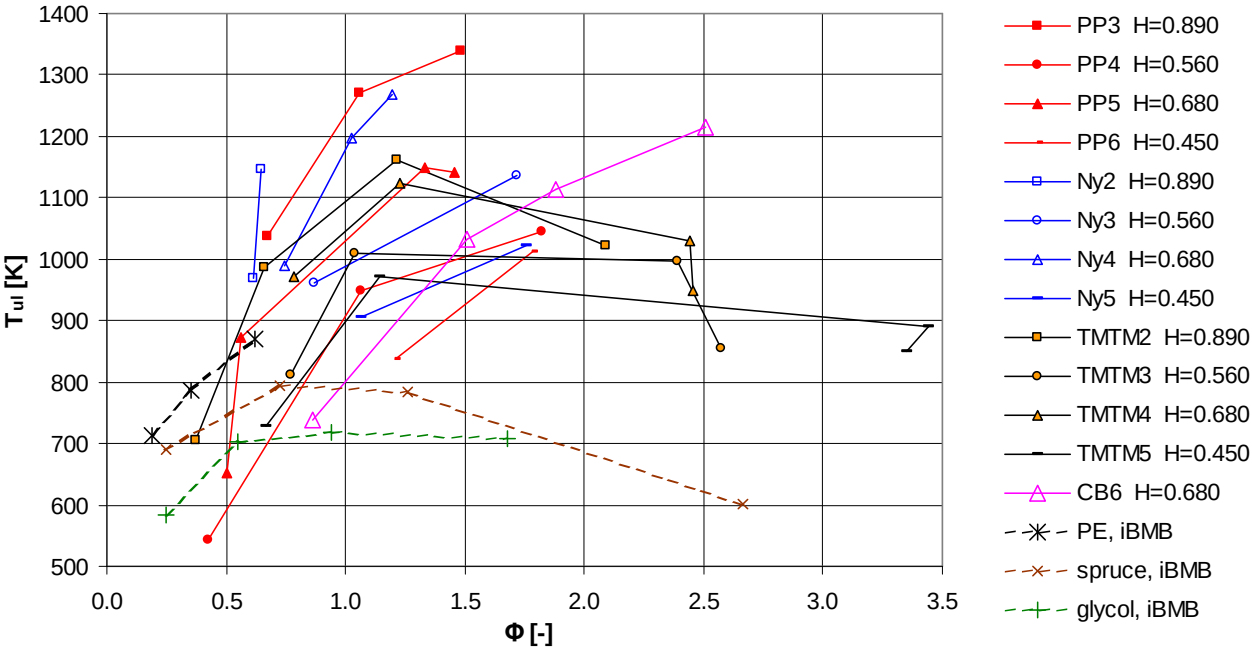

Fig. 2-38. Upper layer temperatures correlated with the amended GER. ISO 9705 compartment data compiled together from the TOXFIRE test series (open dots: opening yields, closed dots: duct yields, data from one test fire is connected) and iBMB test series (data from different test fires with the same fuel is connected by a dotted line).

With exception of the polymer PP and the solvent CB, all CO yields from the TOXFIRE series are conservatively described by the high temperature Equation (2-20b), although sometimes the upper layer temperatures were lower than 900 K. For chlorobenzene, high CO yields are expected (also for well-ventilated conditions), since chlorine acts as a flame

inhibitor in the gaseous phase, where burnout of CO is reduced (Tewarson et al. 1994, Bourbigot and Le Bras 2004). The noticeable behaviour of some elevated CO yields from PP at lower GERs can be attributed mainly to low upper layer temperatures. For PP5, the two points at $\Phi = 0.50$ and $\Phi = 0.56$, result from upper layer temperatures of $T_{ul} = 653$ K and $T_{ul} = 872$ K respectively. The decreased CO yield at $\Phi = 1.33$ is the consequence of reacting upper layer gases at $T_{ul} = 1150$ K. The case for PP4 is similar. The only two data points that contradict Equation (2-20b) are the elevated CO yields from PP3 at $\Phi = 0.67$ with $T_{ul} = 1037$ K and PP4 at $\Phi = 1.06$ with $T_{ul} = 948$ K.

The iBMB series represent the temperature level below $T_{ul} = 800$ K (Fig. 2-38, one exception with PE #16, $T_{ul} = 870$ K). However, the glycol and spruce data is covered by the high temperature Equation (2-20b). Only PE, which is known to generate higher yields than glycol or spruce (cf. Fig. 2-25 and (Tewarson 2002)) is better represented by Equation (2-20a).

It must be pointed out that Gottuk and Lattimer's Equation (2-20b) was established from experiments in a prototype compartment of 2.2 m^3 volume, while the ISO 9705 compartment was 20.7 m^3 in volume and was equipped with window-style (TOXFIRE) and door-style (iBMB) vents. Even so, it can be concluded that this equation in most cases holds true for the qualitative behaviour of CO generation in the ISO 9705 compartment.

Some data of the iBMB experiments indicates that an extension of this equation to a lower temperature level would be justified. On the other hand, some tests showed elevated CO yields at $\Phi \approx 0.5$, which could not be explained with Gottuk and Lattimer's low temperature Equation (2-20a).

Concerning the quantitative behaviour of the CO yields, a distinction must be made between well-ventilated fires (about $\Phi < 0.5$) and under-ventilated fires. For well-ventilated fires, the fuel structure is of major importance. The Equations (2-20a+b), which were derived from hexane-data, may not yield sufficiently conservative CO levels (Tewarson 2002). For under-ventilated fires, Gottuk and Lattimer (2002) reported that the equations "may not provide the maximum levels of incomplete combustion products that can be produced in a fire". The newly compiled data from fires of hydrocarbons and oxygenated hydrocarbons does not exceed the limit of Equations (2-20a+b). For fuels containing hetero-atoms, the situation is different. As already mentioned, higher CO yields are to be expected from chlorobenzene. The oxidation of carbon was less influenced by nitrogen in fires of nylon (63 % carbon content) and sulphur in fires of TMTM (33 % carbon content). This is illustrated by the normalised CO yields (Fig. 2-39), which lie closer together for hydrocarbons and fuels containing nitrogen and sulphur.

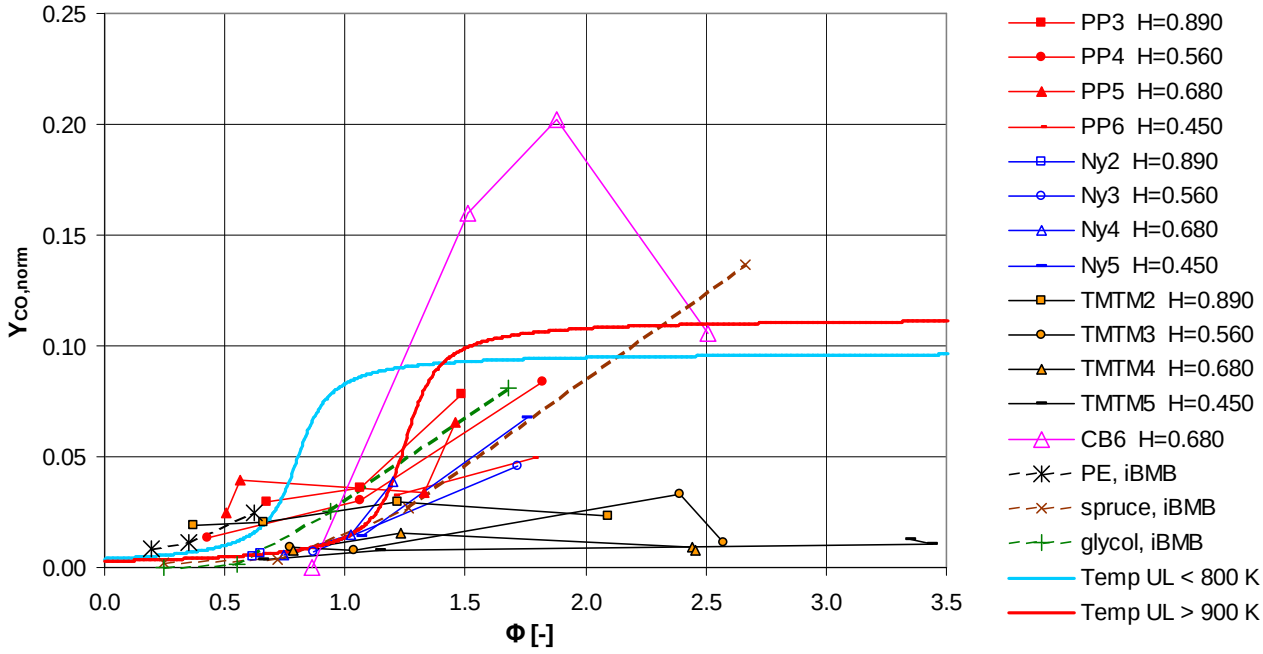

Fig. 2-39. Normalised CO yield correlated with the amended GER. ISO 9705 compartment data compiled together from the TOXFIRE test series (open dots: opening yields, closed dots: duct yields, data from one test fire is connected) and iBMB test series (data from different test fires with the same fuel is connected by dotted line). Comparison with Equations (2-20a+b) calculated for normalised yields of hexane.

In the work discussed so far, typical compartment fires with fuel located at the bottom of the compartment are investigated. The influence of fuel in the upper layer is not treated.

2.4.8.3 Treatment of external combustion

The occurrence of external combustion and the behaviour of the CO yields is also treated in different ways. From his hood experiments, Beyler proposed his ignition index (Eq. (2-16)) to assess layer burning, which takes place at the hood to ambient-air interface. In principle the ignition index is also suited to assess external combustion of exhausting gases.

Zukoski et al. did not study combustion at the boundary of the hood control volume. By injection of additional air into the hood, they showed that combustion inside the hood is controlled by the hood equivalence ratio, instead of the plume equivalence ratio (Fig. 2-6).

Gottuk and Lattimer distinguished between flame extensions and external burning from under-ventilated conditions (Fig. 2-11), but only regarded the latter as a phenomenon to reduce Y_{CO}. They proposed to assess the occurrence of external burning from under-ventilated conditions by the ignition index or by $\Phi_{EC} > 1.6$. As a second precondition to consider CO reduction by external combustion, the smoke layer depth has to be smaller than the lowest elevation of gases leaving the compartment (cf. Fig. 2-12 and Fig. 2-13).

When both preconditions are fulfilled, an extended control volume, that reaches up to the flame tips of the external flames, is considered to determine Φ_{FT}. Application of this methodology is difficult in practice, because the length of the external flame and the entrainment into it must be known.

Pitts did not treat external combustion. Instead, as a process occurring at the opening vent, he reported on CO generation by air entrainment directly into the rich, high-temperature upper layer (Fig. 2-15). This assumption contradicts the above-mentioned findings of Zukoski et al., where CO was reduced by air addition into the hood layer. The structure of vent flows is discussed in Sect. 3.2.1.

From the TOXFIRE large-scale experiments, Lönnermark et al. used external combustion as the criterion for flashover (cf. Sect. 2.4.5). When the reported GER of external combustion $\Phi_{EC,rep}$ (Lönnermark 2005b) is amended for amended mass flows, external combustion occurred between $0.93 < \Phi_{EC} < 2.44$. The highest Φ_{EC} are given for TMTM.

Wieczorek considered both phenomena of external combustion including flame extensions. In his methodology (cf. Fig. 2-33) external combustion is given a different meaning than described by other researchers: usually external combustion is considered to reduce CO yields. Wieczorek used the proportion of flaming combustion within the doorway to correlate the species concentration measured within the flames. Consequently, the CO yields measured in the flames increased. From re-examination (Sect. 2.4.7.2) of his study it can be concluded that flame extensions also influence the final yields.

3 COMPARTMENT FIRE DYNAMICS AND PLUME THEORY

From the literature review, re-examination, and amendments of research work concerning the GER-concept reasonable agreement was achieved regarding the correlation of CO yields with the GER and in addition a temperature dependence is shown. Less consistent understanding is found for the treatment of external combustion. Main conclusions were drawn from hood experiments and small-scale, prototype compartments, which partly do not represent real-scale fires. To close this gap of understanding, the main phenomena are examined in the context of the general cognition of compartment fire dynamics and plume theory.

At the beginning of this chapter, the spectrum of compartment fire characteristics is described and the scope of application of the GER-concept is illustrated. Then the influence of compartment fire dynamics on the relationship between the ventilation conditions of the compartment (GER) with the ventilation conditions of the reacting zones, i.e. the fire plume and possibly the upper layer, is discussed for compartment fires without external combustion. Finally, for compartment fires with external combustion, criteria to assess external combustion are examined and the efficiency of external combustion is discussed.

3.1 Scope of application of the GER-concept

It was shown before that the ventilation factor $w_v * H^{3/2}$ is decisive for the achievable mass flows in compartment fires. Together with the mass loss rate $\dot{m}_f$, which depends on the fuel area A_f and a self-regulating mass loss rate per unit area, the GER of an actual compartment fire is established. However, steady state compartment fires cannot be achieved for every combination of ventilation factor and mass loss rate. Using the example of liquid pool fires in small-scale compartments, different fire regimes depending on the ratio $(w_v * H^{3/2}) / A_f$ can be defined (Fig. 3-1). For small ratios $(w_v * H^{3/2}) / A_f$, the fire extinguishes after ignition, because the air supply is insufficient to sustain a sufficient oxygen concentration close to the fuel source (regime I) (Takeda and Akita 1981, Utiskul et al. 2004). When the ratio $(w_v * H^{3/2}) / A_f$ is increased, a transitional regime II can establish itself, where laminar flaming on a low mass loss rate per unit area may occur (Takeda and Akita 1981). The flames may also lift off the burner and move through the compartment as ghosting flames, before final extinction occurs (Utiskul et al. 2004, Sugawa et al. 1989). When the ratio $(w_v * H^{3/2}) / A_f$ is further increased, a regime III with sustained burning can be reached. This is accompanied by unstable (Takeda and Akita 1981) or steady (Utiskul et al. 2004) flame oscillations and possible burning at the vent

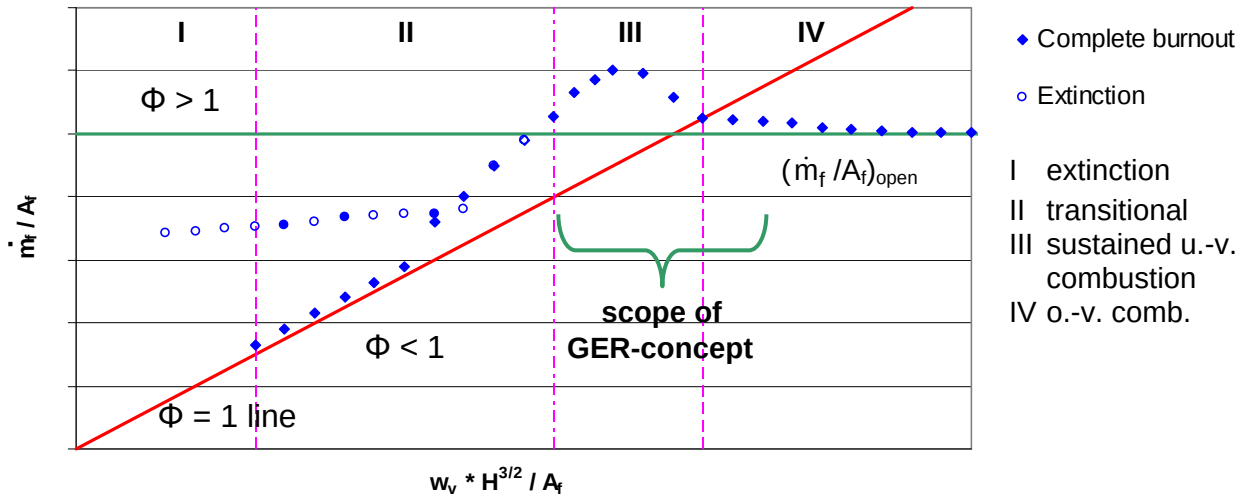

Fig. 3-1. Schematic behaviour of the mass loss rate per unit area $\dot{m}_f / A_f$ in correlation with the ratio $(w_v * H^{3/2}) / A_f$ for liquid fuels. Scope of application of the GER-concept.

including external combustion. When the ratio $(w_v * H^{3/2}) / A_f$ is increased still further, the fire becomes more stable and reaches a regime IV of steady burning (Takeda and Akita 1981, Utiskul et al. 2004), where low frequency oscillating behaviour may occur (Kim et al. 1993). The transition between regime III and IV is the transition between under-ventilated and over-ventilated fires.

Concerning the GER-concept, regime III is of major interest, in which sustained under-ventilated combustion occurs. Additionally, a small part of the open-end regime IV is of interest, where the fire is over-ventilated, but not yet well-ventilated.

In the study of Utiskul et al. (2004) with heptane as fuel, regime III started at a ratio $(w_v * H^{3/2}) / A_f \approx 0.11\ m^{1/2}$ and finished at $(w_v * H^{3/2}) / A_f \approx 0.57\ m^{1/2}$ when the fires became over-ventilated. That means that regime III encompassed a variation in $(w_v * H^{3/2}) / A_f$ by a factor of 5 only. In two other studies with methanol, the ratio $(w_v * H^{3/2}) / A_f$ for regime III varied by 3.9 (Takeda and Akita 1981) and by a factor of similar size (Kim et al. 1993). All studies were performed on a small-scale, thus the influence of larger compartments, e.g. due to increased heat capacity, cannot be evaluated. Within the over-ventilated, but still not well-ventilated area (about $0.5 < \Phi < 1.0$) in regime IV, the mass loss rate per unit area decreases with increasing $(w_v * H^{3/2}) / A_f$. Thus, the variation of the ratio $(w_v * H^{3/2}) / A_f$ is greater than a factor of 2 for $0.5 < \Phi < 1.0$.

For fires of cellulosic fuel, such as wood cribs, mass loss rates per unit area are generally lower than for non-cellulosic fuel (Bullen and Thomas 1979). However, the characteristic of regime IV is qualitatively similar. Regime II, where pool fires may extinguish, is replaced by a smooth transition from regime III to decreased pyrolysis rates per unit area resulting in smouldering fires. This behaviour is attributed to the porous structure and charring of

wood, where the burning surfaces are shielded from the influence of the compartment (Drysdale 1998, p. 331). The applicability of the GER-concept to smouldering fires has not yet been shown. In Fig. 3-1 the theoretical scope of application of the GER-concept is illustrated. For small-scale compartment fires with liquid fuels, the GER-concept can be reasonably applied, when the ratio $(w_v * H^{3/2}) / A_f$ varies by about one order of magnitude. For real-scale fires and fires with solid fuels, it is assumed that the ratio increases, but no systematic data exists.

Gaseous fuels are applied with pre-set fuel supply rates. As can be seen from Wieczorek's propane-fuelled compartment fires, the ventilation factor and the fuel supply rate also have to match for controlled conditions. Wieczorek had to leave out the experiment with the smallest vent width (w_V = 0.076 m) in his methodology, because jet flames established themselves at the exhaust plane and the flow dynamics in the compartment broke down (Sect. 2.4.7.1). This behaviour can be ascribed to a particular type of regime I, because with the fuel pyrolysis rate depending on the heat feedback, the fire was extinguished.

3.2 Compartment fires without external combustion

In this type of fire the pure GER-concept, ignoring external combustion, can be applied. First the main flow dynamics are described and the relationship between different equivalence ratios is illustrated. Then the fire plume behaviour is studied and effects of vitiation and fuel injection in the upper layer are examined.

3.2.1 Mass exchanges in compartment fires

Fig. 3-2 illustrates a well-ventilated compartment fire with an already stratified hot gas layer of combustion products and excess air and a cold gas layer of nearly un-vitiated air. The mass exchanges $\dot{m}_{in}$ and $\dot{m}_{out}$ with the ambient atmosphere were extensively treated in the previous chapter. In this section the mass flows within the compartment are examined. As mixing between a hot layer moving on top of a cooler fluid is relatively inefficient (Drysdale 1998, p. 141, Quintiere 2002), for the relevant mass flows between the upper layer and the lower layer the following processes have to be considered

- the buoyant plume mass flow $\dot{m}_{pl}(z)$ that increases with elevation z,
- the net buoyant flows along the compartment walls $\dot{m}_w$, and
- the feedback flow $\dot{m}_{fb}$ by shear mixing of exhaust gases with incoming air.

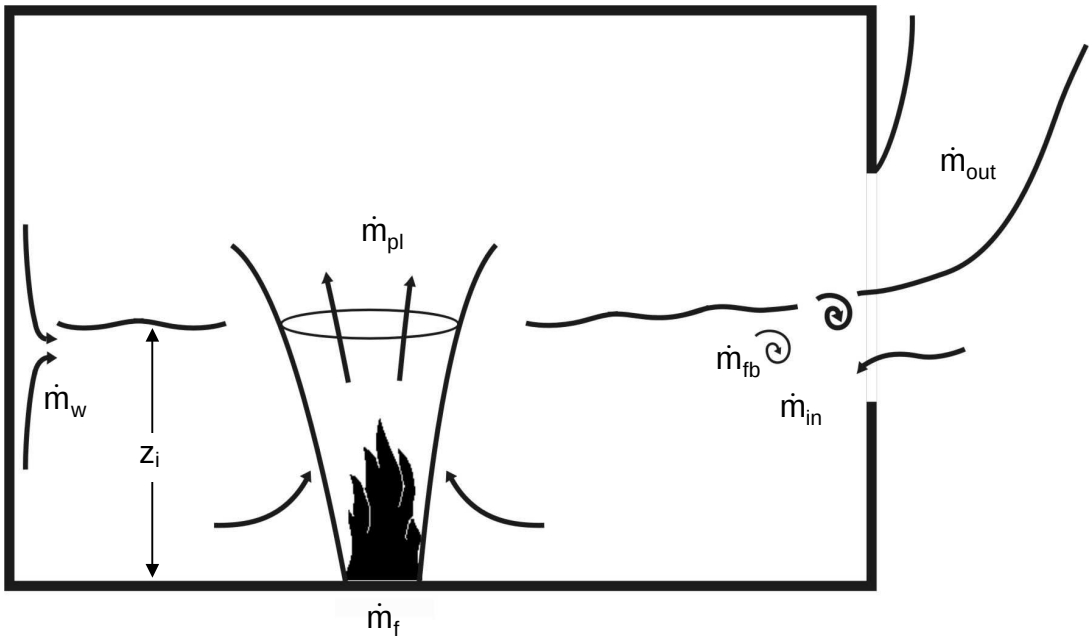

Fig. 3-2. Mass flows in compartment fires without external combustion.

The buoyant fire plume with fuel mass flow $\dot{m}_f$ entrains mass into the flaming zone and above the flame. If the fire source is located at the bottom of the compartment, at the interface height z_i, the plume will immerse into the hot gas layer that will be further filled up with excess air and combustion products. As this process contributes most to the compartment fire ventilation and as most of the reaction occurs within the plume, the plume will be treated more extensively in the next section.

When external combustion does not occur, the plume size is relatively small compared to the compartment volume. For this situation the temperatures and gas concentrations in the hot and cold gas layers are considered to be uniform for many applications. Nevertheless, depending on the thermal properties of the compartment walls, the upper-layer fluid close to the walls will be significantly cooler than the upper-layer average temperature. The lower-layer walls might cool or heat up the lower layer, therefore the net buoyant wall flow $\dot{m}_w$ between the upper and lower layer will usually be directed downwards (Drysdale 1998, p. 298, Quintiere 2002). Under particular conditions, it can also be directed upwards (Dembsey et al. 1995).

The effects of shear mixing of exhaust gases with incoming air at the vent have not yet been sufficiently studied (Jones et al. 2004, p. 34). Vortex shedding at the shear layer causes a feedback flow $\dot{m}_{fb}$ which is entrained into the incoming air flow and thus vitiates the air in the lower layer. Quintiere (2002) suggested that the flow rate of the remixed stream can be significant relative to the vent flow rate especially for small exhaust vents. This assumption is confirmed by a series of methane-fuelled compartment fires conducted by Steckler et al. (1982). When they altered the width of a door vent and a window vent,

for the quasi-steady state they estimated the upper limit of feedback flows $\dot{m}_{fb,max}$ into the lower layer by the energy balance of the lower layer

$$\dot{m}_{fb,max} = \dot{m}_{in} \cdot (T_{ll} - T_a) / (T_{ul} - T_{ll}) \quad (3\text{-}1)$$

As the heat transfer from the upper layer and the lower compartment surfaces to the lower layer gases was disregarded, the calculated feedback flow represents the upper limit.

From the data of Steckler et al. the maximum feedback flows relative to the air inflows plus feedback flows

$$\dot{m}_{rel,fb,max} = \dot{m}_{fb,max} / (\dot{m}_{in} + \dot{m}_{fb,max}) \quad (3\text{-}2)$$

were calculated and correlated with the reported heat release rates, relative vent sizes and calculated GERs (Fig. 3-3a-c). The *door* vent was altered in width from 1/6 to 8/6 (6/6 = 0.74 m * 1.83 m) while the *window* vent was altered in height of the window-sill from 1/3 to 3/3 (3/3 = 0.74 m * 1.38 m).

Fig. 3-3 illustrates that the relative feedback flow is nearly independent of the heat release rate (a), while it is negatively correlated with the vent size (b) and positively correlated with the GER (c). The correlation of the feedback flow with the *door* size might be a side effect of the correlation with the GER. As the height of the *window* is altered, the size of the shear area relative to the vent size is increased by decreasing the window size. This is not the case for the door vent because it is altered in width. Therefore the correlation of the relative feedback flow with the window vent size is even more evident than with the door

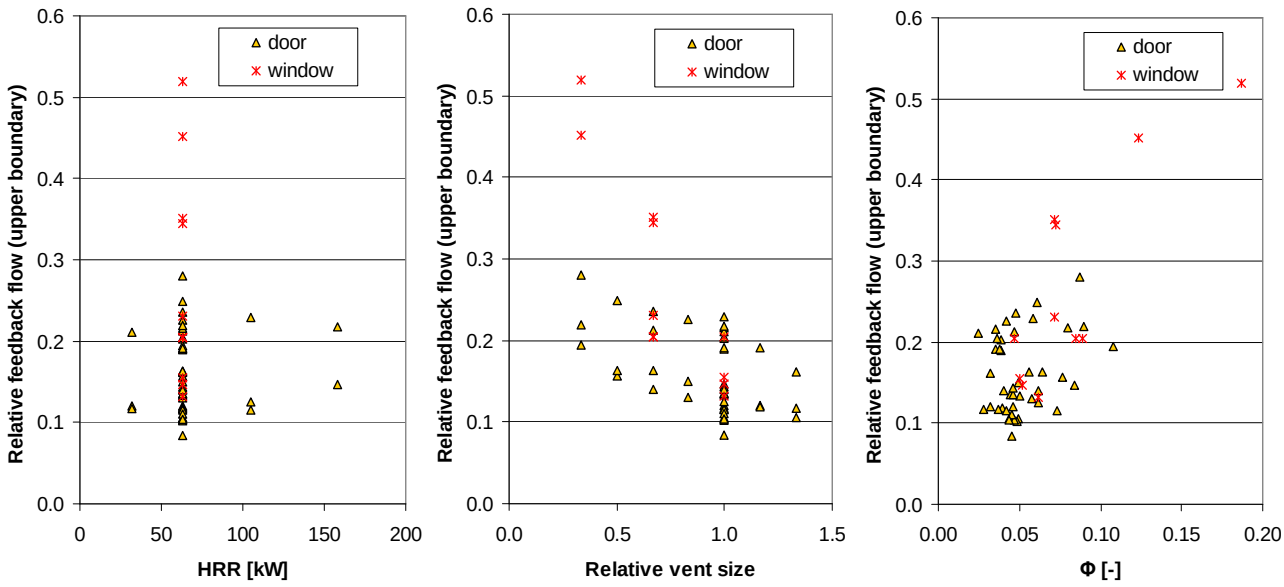

Fig. 3-3a-c. Upper boundary of the relative feedback flow $\dot{m}_{rel,fb,max}$ in correlation with the heat release rate (a), relative vent size (b), and the GER (c) (calculated from data of Steckler et al. (1982)).

vent size (Fig. 3-3b). For window vents the estimated upper limits of the feedback flows were 13 percent for the tallest window configuration (lowest sill height) and 52 percent for the lowest window configuration (highest sill height). The upper limits of the relative feedback flows were estimated to be up to 10 percent for the largest door-width and 28 percent for the smallest door-width.

Much smaller feedback flows were reported by Dembsey et al. (1995) for propane-fuelled compartment fires at quasi-steady state. The compartment of 2.5 m * 3.7 m * 2.5 m height was equipped with a constant 0.76 m * 2.0 m door vent centrally located in one of the shorter walls. The wall surfaces consisted of 19 mm plywood with two layers of insulating linings, which were finally coated by 0.8 mm stainless steel sheets. The fuel supply rates were increased by steps and global equivalence ratios from 0.14 to 0.35 were reached. The reported relative shear mixing feedback flows $\dot{m}_{rel,fb}$ range from 2.9 percent to 4.6 percent, again with a positive correlation to the GER (Fig. 3-4a). The correlation to the heat release rate (b) is attributed to a nearly linear correlation of HRR and GER (at constant vent size).

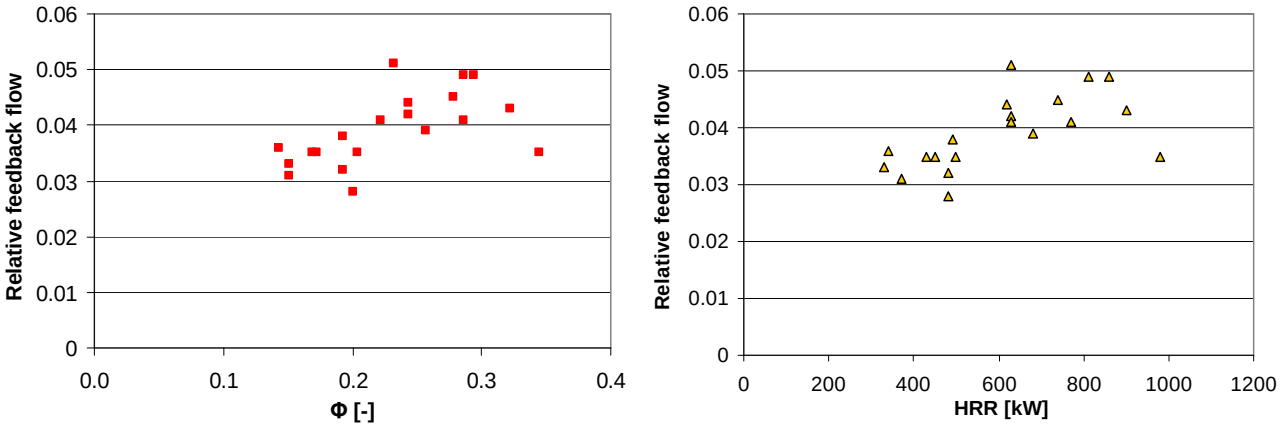

Fig. 3-4a+b. Relative feedback flow $\dot{m}_{rel,fb}$ in correlation with the GER (a) and the heat release rate (b) (data taken from Dembsey et al. (1995)).

The mass flows $\dot{m}_{fb}$ and $\dot{m}_{w}$ do not occur in hood experiments, from where some of the data on CO yields correlated with the GER is derived. Therefore it should be examined whether the flow dynamics of hood versus compartment experiments have an effect on CO generation. First the influence on the different equivalence ratios is illustrated:

If the plume mass flow is the only flow between the lower and the upper layer, the upper layer equivalence ratio (ULER) will represent the time history of the ventilation of the plume. For steady state conditions (steady state HRR and interface height z_i), the ULER will equal the plume equivalence ratio (PER) averaged over the gas flow that penetrates the interface height z_i

$$\phi_{pl}(z_i) = \phi_{ul} = \phi \qquad (3\text{-}3a)$$

Both ratios will additionally equal the GER, as the only outflow from the compartment is from the upper layer.

When taking into account the net buoyant flows along the compartment walls $\dot{m}_w$ and feedback flows $\dot{m}_{fb}$, both these flows will mostly be directed against the direction of the plume mass flow. The downward flows $\dot{m}_{fb}$ and $\dot{m}_w$ vitiate the lower layer, while the circulation is closed by the plume. Although this will lead to an increased plume mass flow relative to the compartment external ventilation, it does not invalidate Eq. (3-3a), because the additional plume mass flow has the same equivalence ratio as the upper layer. As lower layer vitiation by $\dot{m}_{fb}$ and frequently $\dot{m}_w$ does not result in a change of the GER, a possible effect of a vitiated lower layer in compartment fires on the species yields will be examined separately in Section 3.2.3.

In the less relevant case of net upward flows along the compartment walls $\dot{m}_w$ there is additional air inflow into the upper layer. Therefore the ULER will be lower than the PER averaged over the penetrating plume area at the interface height z_i

$$\phi_{pl}(z_i) \geq \phi_{ul} = \phi \qquad \text{(3-3b)}$$

When only the plume is taken as the reacting zone (e.g. $T_{ul} < 800$ K), the correlation of species yields with the GER will over-estimate the actual ventilation conditions.

The only available data to quantify the deviation of PER and GER from these special conditions is given by Dembsey et al. (1995) from the tests described above in a compartment that was coated by steel sheet on top of insulating layers. They reported upwards wall flows of 0.17 kg/s for 330 kW heat release rate decreasing to 0.12 kg/s for 900 kW heat release rate. The calculated PER is between 0.03 and 0.05 greater than the reported GER for the observed range of ventilation. It is indicated in Fig. 3-5 by the

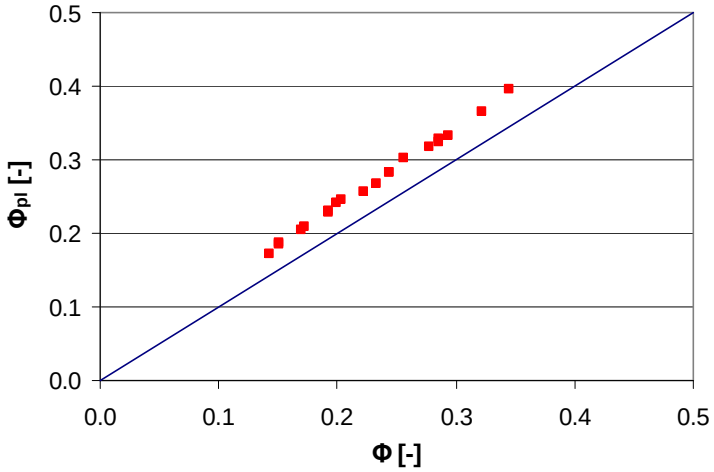

Fig. 3-5. Plume equivalence ratio in correlation with the global equivalence ratio (calculated from data of Dembsey et al. (1995)).

deviation of the dots from the line $\Phi_{pl} = \Phi$. This increase is too small to have a significant influence on CO yields. However, if the thermo-physical properties of a fire compartment might further increase upwards wall flows, the deviation of PER to GER will reach significant values. On the other hand it will also be shown (Sect. 3.2.2.3), that for equivalence ratios over approximately 0.5, which are relevant in terms of the GER-concept, the lower layer might no longer cover the complete compartment floor. In this case wall flows between both layers lose significance.

The considerations above show that examination of the fire plume properties will give important information about compartment fire ventilation conditions. In most cases the PER characterises the ULER quite reasonably (Eq. (3-3a)). Plume behaviour was studied by many researchers and is represented by empirical plume equations.

3.2.2 Properties of the fire plume

3.2.2.1 General characteristics of fire plumes

A fire plume consists of three different regions:

1. a region above the burner/fuel bed surface in which there is a persistent flame and an accelerating flow of burning gases (the persistent flame zone)
2. a region of intermittent flaming and near-constant flow velocity (the intermittent zone), and
3. the buoyant plume which is characterised by decreasing velocity and temperature with height (buoyant plume zone).

Because of the intermittent flame characteristic, the (mean) flame height z_{fl} is commonly defined as the height where the flame is observed 50 % of the time by visual, or better, video observations (Beyler 1986b, Zukoski 1995). Regarding the entrainment characteristics, the region below the flame height is denoted near field and the region above is termed far field, respectively.

From the elevation of the flame height z_{fl} relative to the interface height z_i three modes can be distinguished (Zukoski 1995):

- the first mode, where the flame is completely immersed in the lower layer ($z_{fl} < z_i$)
- the second mode, where combustion occurs in a two-layer configuration ($z_{fl} > z_i$)
- the third mode, where the flame is completely immersed in the upper layer ($z_{fl} >> z_i$, $z_i \rightarrow 0$)

These modes are known to influence the flame shape and species generation of fires. In the following sections, using the theories of flame height and mass entrainment into fire plumes, these modes are correlated with the GER according to Equation (3-3a).

3.2.2.2 Scaling parameters and flame height correlations

Different types of fire plumes are characterised by the non-dimensional Froude number Fr. It can be considered as the ratio of inertia to buoyancy forces in the system and is conventionally expressed as

$$Fr = \frac{v^2}{g \cdot D} \tag{3-4}$$

where v is the velocity of the gases and g is the acceleration due to gravity. The characteristic dimension D is given by the fuel bed / burner diameter, or for non-circular fuel beds / burners it is defined by the effective diameter of the same fuel / burner surface area A_f:

$$D = 2\sqrt{\frac{A_f}{\pi}} \tag{3-5}$$

Jet flames are dominated by the initial momentum of the fuel stream and therefore associated with Froude numbers exceeding Fr = 100 (Cox 1995). In contrast, in natural fires buoyancy is the predominant driving force with very small initial velocity of the fuel vapours. The average initial velocity of the fuel vapours can be estimated from the fuel pyrolysis rate per unit area. However, the velocity is commonly expressed as the heat release rate per unit area of the fuel bed taking the fuel density into consideration

$$v = \frac{\dot{Q}}{\Delta H_c \cdot \rho_f (\pi \cdot D^2 / 4)} \tag{3-6}$$

From this equation a proportionality can be seen for the heat release rate with the square root of the Froude number

$$\sqrt{Fr} = K_1 \cdot \sqrt{\frac{\dot{Q}^2}{D^5}} = K_1 \cdot \frac{\dot{Q}}{\sqrt{D} \cdot D^2} \tag{3-7}$$

where K_1 is a constant composed of fuel properties (ΔH_C, ρ_f) and the acceleration due to gravity.

The non-dimensional heat release rate $\dot{Q}^*$ is also proportional to the square root of the Froude number. This parameter was introduced by Zukoski and is most frequently used in fire safety science to correlate plume properties of different kinds of fire plumes

$$\dot{Q}^* = \frac{\dot{Q}}{\rho_\infty \cdot c_p \cdot T_\infty \cdot \sqrt{g \cdot D} \cdot D^2} = K_2 \cdot \frac{\dot{Q}}{\sqrt{D} \cdot D^2} \tag{3-8}$$

The density ρ_∞, the heat capacity c_p, and the temperature T_∞ of ambient air as well as the acceleration of gravity are constants to be expressed by $K_2 \approx 9.04 * 10^{-4}$ $m^{5/2}/kW$.

In reviews of various flame height correlations (Heskestad 2002, McCaffrey 1990, Beyler 1986b) the ratio z_{fl} / D is related to the non-dimensional heat release rate (Fig. 3-6). The data on the low $\dot{Q}^*$ end represents pool fires with flame heights of the same order of magnitude as the diameter. This data is less consistent than the middle and right part of Fig. 3-6 which was attributed to fuel source geometry (Beyler 1986b) or to the laminar character of laboratory scale flamelets (McCaffrey 1990). The correlations of Cox & Chitty (1985) provide data in between the correlations of Zukoski and Becker & Liang:

$$\frac{z_{fl}}{D} = 15.1 \cdot \dot{Q}^{*2} \qquad \text{for} \quad 0.13 < \dot{Q}^* < 0.28 \tag{3-9}$$

and

$$\frac{z_{fl}}{D} = 3.2 \cdot \dot{Q}^* \qquad \text{for} \quad 0.28 < \dot{Q}^* < 0.55 \tag{3-10}$$

The intermediate regime is well represented by Heskestad's equation (1983) which also covers small $\dot{Q}^*$ and which can be written in the form

$$\frac{z_{fl}}{D} = -1.02 + 3.7 \cdot \dot{Q}^{*2/5} \qquad \text{for} \quad 0.12 < \dot{Q}^* < 1.2 \cdot 10^4 \tag{3-11}$$

Since most accidental fires were characterised by $\dot{Q}^*$ to be less than 10 (Zukoski 1995, Ma and Quintiere 2003), the Equation (3-11) is satisfactory for high $\dot{Q}^*$ accidental fires.

For comparison the correlations of McCaffrey (1983) for the persistent flame height $z_{fl,per}$ and the intermittent flame height $z_{fl,int}$ are additionally illustrated in Fig. 3-6

$$\frac{z_{fl,per}}{D} = 1.3 \cdot \dot{Q}^{*2/5} \tag{3-12}$$

and

$$\frac{z_{fl,int}}{D} = 3.3 \cdot \dot{Q}^{*2/5} \tag{3-13}$$

Although no restriction to a certain range is given, these equations represent by definition the lower and higher boundary of the mean flame height z_{fl}.

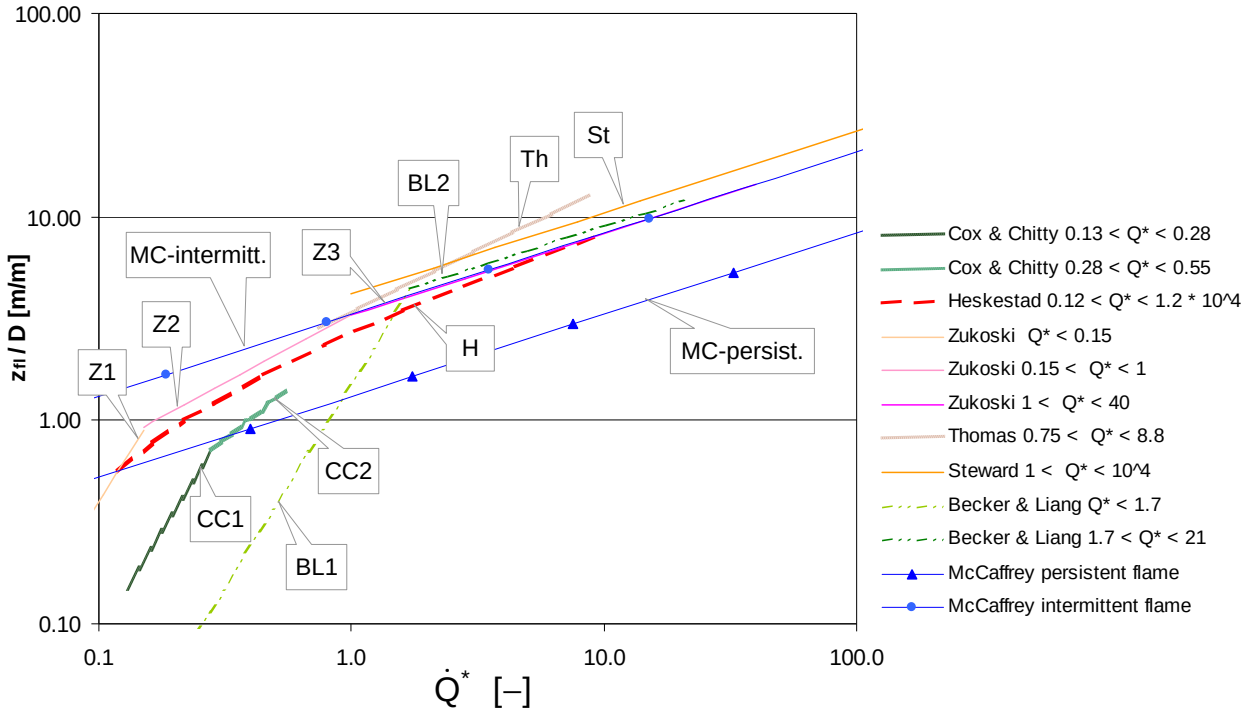

Fig. 3-6. Mean flame height correlations of various researchers compiled by McCaffrey (1990), also presented by Heskestad (2002). The correlations of McCaffrey (1983) for the persistent and intermittent flame height are added for comparison. Double logarithmic scale.

3.2.2.3 Mass entrainment and combustion in the fire plume

Entrainment models, which describe the plume mass flow as a function of the elevation over the fuel bed, are given with different scaling parameters (Zukoski 1995). However, well accepted plume mass flow correlations were given by McCaffrey (1983), which were later confirmed by Dembsey et al. (1995) and which are implemented in the CFAST zone model (Jones et al. 2004). They can be written as:

for the persistent flame:

$$\dot{m}_{pl} = 0.011 \cdot z^{0.566} \cdot \dot{Q}^{0.774} \qquad \text{for} \quad 0 < z/\dot{Q}^{2/5} < 0.08 \tag{3-14}$$

for the intermittent flame:

$$\dot{m}_{pl} = 0.0026 \cdot z^{0.909} \cdot \dot{Q}^{0.636} \qquad \text{for} \quad 0.08 < z/\dot{Q}^{2/5} < 0.20 \tag{3-15}$$

In order to express the air entrainment over the flame height, McCaffrey's Equation (3-12) for the permanent flame height can be expressed by the heat release rate by introducing Equation (3-8). When the fuel mass flow is additionally introduced, the equation becomes

$$z_{fl,per} = 0.08 \cdot \dot{Q}^{2/5} = 0.08 \cdot (\dot{m}_f \cdot \Delta H_{c,eff})^{2/5} \quad (3\text{-}16)$$

The plume mass flow (Eq. (3-14)) originates from the fuel mass flow plus entrained air. If the heat release rate is expressed by the fuel mass flow, the ratio

$$\frac{z}{z_{fl,per}} = \frac{(m_f \cdot (1 + r_{air} / \phi_{pl}))^{1/0.566} \cdot (m_f \cdot \Delta H_{C,eff})^{-0.774/0.566}}{0.08 \cdot 0.011^{1/0.566} \cdot m_f^{2/5} \cdot \Delta H_{C,eff}} \quad (3\text{-}17)$$

can be recast to express the entrainment number N over the elevation z

$$N(z) = 1/\phi_{pl}(z) = \left(\left(\frac{z}{z_{f,per}} \right)^{0.566} \cdot 0.0026 \cdot \Delta H_{C,eff} - 1 \right) / r_{air} \quad (3\text{-}18)$$

For a typical r_{air} = 14.3 and effective heat of combustion of $\Delta H_{C,eff}$ = 32000 kJ/kg, the entrainment over the flame height is illustrated in Fig. 3-7. At the permanent flame height, air entrainment is calculated to be about 5.8 times the value for stoichiometric combustion (Φ_{pl} = 0.17). This value agrees with Ma and Quintiere (2003), who from their review found N for the mean flame height to vary between 5 and 15.

From the Fig. 3-7 it can be seen that stoichiometric entrainment occurs at the very base of the flame. For the circumstances which are relevant in terms of increased CO generation (e.g. Φ_{pl} > 0.5, N < 2), the interface height z_i must have decreased to less than about 15 % of the permanent flame height $z_{fl,per}$. Regarding the three modes which are defined by Zukoski by the ratio z_{fl} to z_i (Sect. 3.2.2.1), only the transition area between modes two and three and the third mode are of interest concerning the GER-concept. The influence of the upper layer on flame behaviour is discussed in the following section.

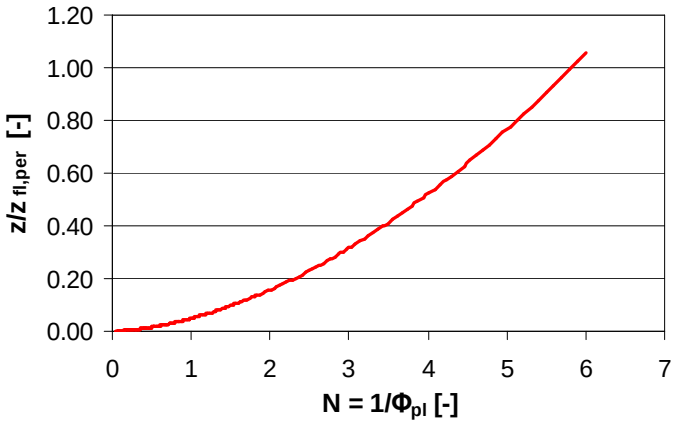

Fig. 3-7. Entrainment number over the flame elevation relative to the persistent flame height. Calculated based on McCaffrey's (1983) plume equations.

Smith and Cox (1992) reported on main species measurements at various locations of a 47 kW buoyant turbulent diffusion flame from a 0.3 m square natural gas burner. From the

data the local equivalence ratio and local combustion efficiency for this $\dot{Q}^*$ = 0.64 fire were calculated. The results are given in (Fig. 3-8a+b) in correlation with the distance from the plume centreline and the elevation z normalised by the flame height z_{fl}. From Fig. 3-8a it can be seen that only the core of the flame is under-ventilated. At the flame tip, the LERs of about 0.2 for the centreline and about 0.1 for the edges agree with the data reported above. Regarding the combustion efficiency (Fig. 3-8b) the heat is predominately released at the lower part of the flame. These results correspond to experiments of Santo and Delichatsios (1984) with turbulent propane pool fires of 0.3 < $\dot{Q}^*$ < 0.5. They reported that nearly all of the heat is released from the lower half of the flame height for pool fires, while for jet flames it is released uniformly along the extent of the flame. This observation confirms that CO generation of accidental fires is only increased when the flames are deeply immersed into the upper layer.

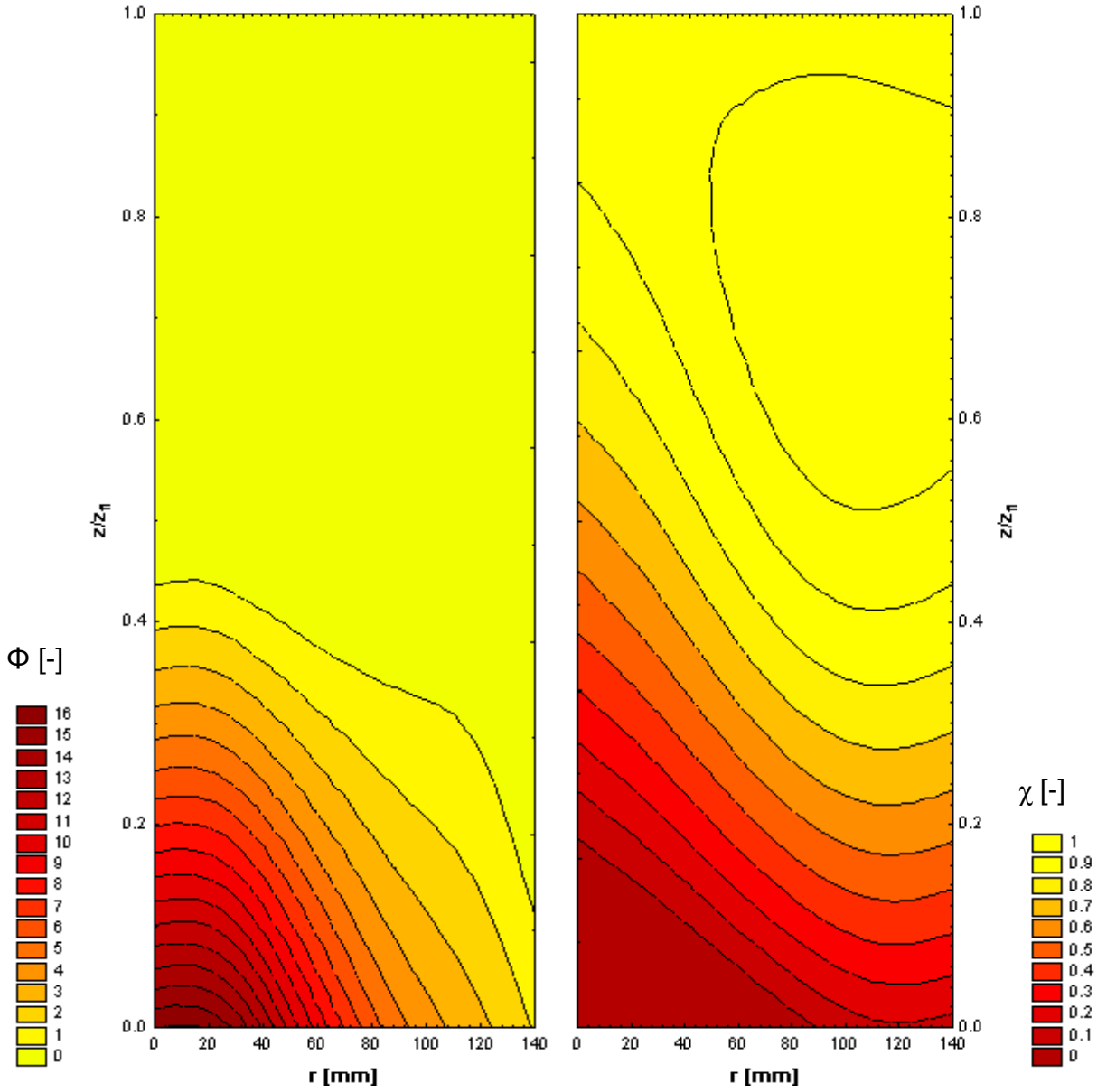

Fig. 3-8a+b. Local equivalence ratio (a) and local combustion efficiency (b) as a function of the location in a $\dot{Q}^*$ = 0.64 natural gas flame (calculated from data of Smith and Cox (1992)).

3.2.2.4 Behaviour of a flame immersed in the upper layer

The behaviour of the flame when it is immersed in the upper layer is not treated in general reviews of plume properties such as (Heskestad 2002, McCaffrey 1990, Beyler 1986b). In fact, Zukoski (1995) mentioned in his extensive treatise that “data on the effects of the upper layer on the fire plume geometry have not been published”. He reported observations that at ULER greater than 1.5, the visual flame height will be reduced compared to the flame height in fresh air and that soot production will be noticeably increased. Close to extinction, soot production is stopped and the flame appears faintly grey-blue and may periodically lift off the burner. In contrast, Morehart, Zukoski, and Kubota (1991) related their observations from hood experiments concerning the oxygen concentration in the upper layer. They reported the flame length to *increase* by about 5 % as the mass fraction of oxygen decreased from the value in air to the extinction limit (measured between $X_{O2} = 0.124$ and $X_{O2} = 0.143$ for natural gas and ethylene). The observation about termination of soot production close to extinction is confirmed.

The fact that descriptions of the behaviour of the burner flame are rare and contradictory might reflect the fact that the experimental situation is somewhat artificial for the representation of accidental compartment fires. Based on the heat balance in a compartment, it has been shown by Babrauskas (1980) that equivalence ratios higher than 0.4 typically lead to flashover conditions. Then the fire will spread over all available fuel and plume theory loses its applicability, as the reaction will take place at any interface of streams of fuel and oxidiser under locally ignitable conditions.

In this context Drysdale (1998, p. 300) reported layer burning starting from an equivalence ratio exceeding 0.8 to 1.0, which is apparently a misreading of Beyler’s data: Beyler mentioned these numbers as the largest values of the *ignition index* where no layer burning occurred. In Beyler’s (1984) experiments an ignition index of 0.8 corresponded to an equivalence ratio of about 1.5. Layer burning was reported to start from $\Phi \approx 1.7$ (cf. Sect. 2.4.1 and 3.3.1.3).

Since the observations mentioned above were related to the equivalence ratio, the oxygen concentration or the ignition index, respectively, possible scenarios are discussed by the following example. In a compartment fire with the fuel source located at the floor, with increasing fuel supply rate, the flame will be immersed in the upper layer when the plume is about 10 times over-ventilated ($\Phi = 0.1$). At this time the combustion efficiency is relatively high at χ_{wv}, so that the upper layer will consist mostly of excess air and combustion products. From the time history, the ULER will be slightly smaller than the GER. With the GER further increased by about 0.5, with a combustion efficiency of e. g. $\chi_{wv} = 0.9$ and the production of intermediate products and smoke neglected, a fire of polyethylene ($(C_2H_4)_n$) will feed the upper layer with a quite inert mixture of $X_{N2} = 0.763$,

X_{CO2} = X_{H2O} = 0.061, X_{O2} = 0.112, and X_{C2H4} = 0.003. As the inert upper layer mixture will be entrained into the upper part of the flaming plume, the decreased combustion efficiency can be explained by self-extinction of the fire plume by nitrogen and combustion products. At a steady state fuel supply rate, this process of combustion under vitiated conditions leads to a certain amount of unburned species in the upper layer, as demonstrated in hood experiments (Sect. 2.4.1 and 2.4.2). The combustion efficiency is also reduced, where a temperature dependence exists (Fig. 3-9).

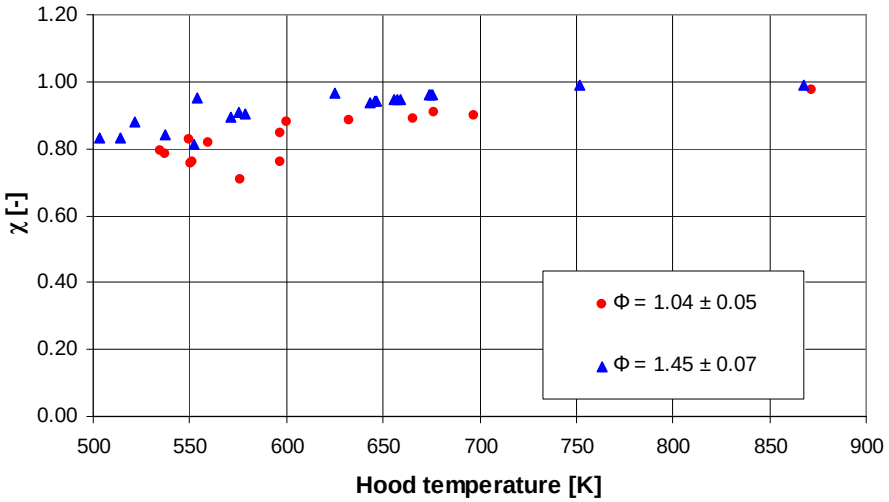

Fig. 3-9. Combustion efficiency χ over the hood temperature at Φ = 1.04 ± 0.05 and Φ = 1.45 ± 0.07. The efficiency is normalised by the ideal value of 0.96 for Φ = 1.04 and 0.69 for Φ = 1.45 (cf. Eq. (2-3b)) (calculated by oxygen depletion calorimetry from data of Zukoski et al. (1991) (cf. Fig. 2-7 and Fig. 2-8)).

With the GER still further increased, an increased amount of unburned species and excess air in the upper layer at increased temperatures in turn diminishes the capability of the upper layer gases to extinguish the fire plume. Obviously this effect is over-compensated by the fact that the flame is more deeply immersed in the upper layer, and that the ratio of entrained mixture of the lower layer to mixture of the upper layer is decreased. The scenario has two possible endpoints:

a) the flame will become completely immersed in the upper layer and will be extinguished by upper layer gases. This process can be assigned to the regime I as described in Sect. 3.1.

b) because of the reduced combustion efficiency the upper layer mixture will become fuel rich at Φ > 1 and reaction will take place at any interface as layer burning or external burning under locally ignitable conditions. This process can be assigned to the regime III as described in Sect. 3.1.

In particular the second endpoint is accompanied by oscillating behaviour before new reaction zones stabilise.

3.2.3 Vitiation studies

3.2.3.1 Phenomenon

It was shown from the plume characteristics that species production correlates with the degree to which the flame is immersed into the upper layer, when the base of the flame entrains unvitiated air. The phenomenon is perfectly illustrated by the results of hood experiments which stand for a simplified compartment. Some results of real compartment fires showed an increase of the CO yields at relatively low GERs, which could not be fully assigned (Fig. 2-37). Therefore the possible influence of vitiation in compartment fires with un-reactive upper layers should be studied. Two different circumstances are considered:

a) Feedback flows and wall flows from the upper layer into the lower layer may vitiate the lower layer mixture (Fig. 3-2). Under these circumstances Equation (3-3a) is still valid, but the oxygen concentration in the lower layer is reduced compared to pure air.

b) In contrast to the typical set-up in fire tests, the fuel source is not located at the lower part of the compartment, but the fuel will be (partly) released directly in the vitiated upper layer. This will happen for example in a storage fire.

3.2.3.2 Review of vitiation studies

In studies applying the GER-concept the effect of entrainment of vitiated air at the flame base has never been treated separately – a point that was also deplored in a recent literature review by Gotoda and Saso (2003). Effects of vitiation were examined in three notable studies:

Santo and Delichatsios (1984) studied turbulent propane pool fires from 30 kW to 50 kW in an apparatus which was supplied with air or vitiated atmospheres which were generated by either one or two separate propane furnaces. The vitiated conditions are given in Table 3-1.

Table 3-1. Vitiated mixture conditions in the study of Santo and Delichatsios (1984).

	X_{O2}	X_{CO2}	X_{H2O}	T
Ambient air	0.210	-	-	25℃
One furnace	0.191	0.010	0.020	40℃
Two furnaces	0.175	0.018	0.031	45℃

At a given heat release rate the flow rate of CO above the flame was measured and no dependence on the degree of vitiation was found. Radiation per unit height decreased significantly with increasing vitiation. Also soot production decreased which was attributed to lower adiabatic flame temperatures at increased vitiation.

Mulholland et al. (1991) used a Cone Calorimeter modified to a Controlled Atmosphere Calorimeter (NIST version, cf. (Babrauskas 2002)) for vitiation studies with different fuels with nitrogen diluted in the air inflow. The air flow was kept constant to maintain a well-ventilated compartment where the GER was always lower than 0.30. Vitiation ranged from pure air to an N_2-enriched mixture which led to extinction. For four solid fuels (ABS, PE, PMMA, and Douglas fir) they found consistent results (Fig. 3-10) for the CO yield that could be expressed by the empirical relation

$$Y_{CO} = Y_{CO,wv} \exp\left(2.7 \frac{X_{O2}^{\infty} - X_{O2}}{X_{O2}^{\infty}} \right) \tag{3-19}$$

where X_{O2} is the actual oxygen mole fraction at vitiated conditions.

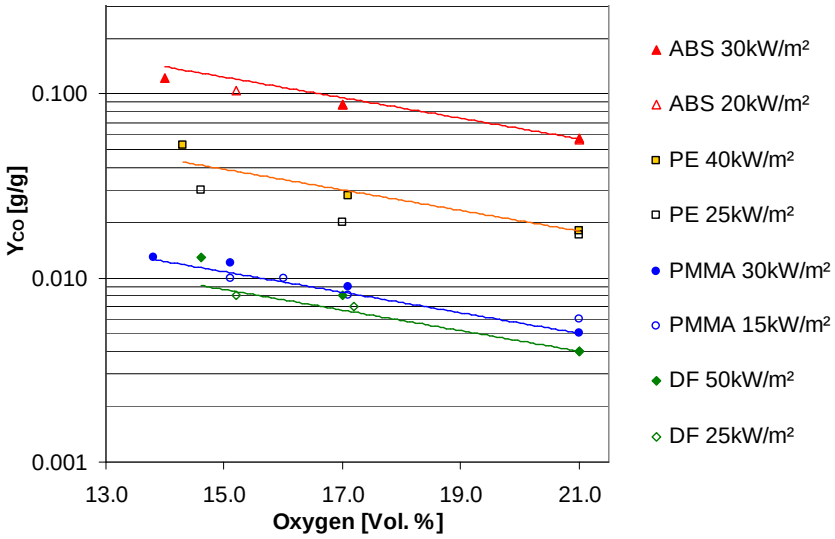

Fig. 3-10. CO yields for solid fuels as a function of O_2 concentration. Fitting by Equation (3-19) (reproduced from Mulholland et al. (1991)).

The exponential behaviour indicates that a significant increase of CO production occurred under highly vitiated conditions close to extinction - a degree of vitiation which was not covered in the study of Santo and Delichatsios. Limiting oxygen concentrations were found between X_{O2} = 0.138 (PMMA) and X_{O2} = 0.152 (Douglas fir). When CO_2 was used as a diluent, the impact on the CO yields increased slightly due to the higher molar heat capacity of CO_2 compared to N_2. However, close to extinction the CO yields are similar for N_2 and CO_2, as the limiting oxygen concentration also depends on the diluent. The soot yields studied by Mulholland et al. were less sensitive to the oxygen concentration than the

CO yields. Soot yields decreased slightly with decreasing oxygen concentration for oxygen-containing fuels (PMMA, Douglas fir), remained constant for PE, and apparently went through a minimum at X_{O2} = 0.17 for ABS.

A study by Tsuchiya and Mathieu (1991) was performed with plywood in the Ohio State University Heat Release Rate Apparatus (OSU-Apparatus). Similar to the Controlled Atmosphere Calorimeter, this apparatus represents a closed system with the sample probe exposed to controlled radiation and pyrolysis gases ignited by a pilot flame. The furnace was supplied with air that was partly diluted with nitrogen to reduce oxygen content from 21 to 8 % volume fraction. In contrast to Mulholland et al., the total oxygen inflow was reduced by reduced oxygen concentration. But through the feedback on the mass loss rate, the GER remained relatively constant in the order of 0.3 for all experiments. Since this study also included oxygen levels where non-flaming combustion occurred (between X_{O2} = 0.13 at heat flux of 30 kW/m^2 and X_{O2} = 0.08 at 50 kW/m^2), a transition point is reported where CO generation increased more than ten-fold. At oxygen concentrations above this transition point the CO generation in terms of the CO/CO_2 ratio increased less than two-fold compared to the level for unvitiated conditions. The decrease of smoke production was also more significant for slightly vitiated atmospheres.

The three studies were performed for different purposes in different small-scale apparati and with different fuels. However, concerning CO formation the studies exhibit the same trend, that no significant increase of CO production is found unless the oxygen concentration is reduced to a value close to the extinction limit. A noted decrease in soot generation under increased vitiation (propane and plywood) is only partly confirmed in the study by Mulholland et al. as different observations were made for different fuels. The reported effects on radiation are consistent with the general literature.

3.2.3.3 Examination of the influence of vitiation

To examine the influence of phenomenon (a) (Sect. 3.2.3.1), the mass flows from the upper to the lower layer must be known, in order to calculate the degree of vitiation in the lower layer. The maximum effect is evaluated by a conservative assessment. In hood experiments the smallest reported GER where CO production increased was 0.5 (cf. Sect. 2.4.1 and 2.4.2). At Φ = 0.5, assuming ideal combustion of polyethylene ($(C_2H_4)_n$), 50 % of oxygen will be depleted and diluted with combustion products, generating an upper layer mixture with X_{O2} = 0.101. The highest value of the maximum relative feedback flows (Equation (3-2)) was $\dot{m}_{rel,fb,max}$ = 0.52 – a value much higher than reported in other studies. This value also includes possible downwards wall flows (cf. Sect. 3.2.1). If both conservative assumptions are combined, the lower layer oxygen concentration becomes:

$$X_{O2} = (\dot{m}_{in} \cdot (X_{O2}^{\infty} + \dot{m}_{rel,fb,max} \cdot 0.101)) / (\dot{m}_{in}(1 + \dot{m}_{rel,fb,max})) = 0.173 \quad (3\text{-}20)$$

For this degree of vitiation, the strongest sensitivity of the CO yields was reported in Mulholland's study. By using their Equation (3-19), the increase in the CO yields is only 1.6 times based on $Y_{CO,wv}$. By this conservative examination, the possibility that the particular flow dynamics in compartment fires lead to a significant increase of CO yields compared to results of hood experiments can be ruled out. Also from the results of the TOXFIRE ISO 9705 experiments no increased CO yields can be seen at smaller vent heights H which lead to increased relative feedback flows (cf. Fig. 2-37).

The examination of phenomenon (b) (Sect. 3.2.3.1), where fuel is (partly) released into the upper layer is straightforward. At Φ = 0.5, assuming again ideal combustion of polyethylene, the upper layer consists of X_{O2} = 0.101. If the upper layer is considered perfectly stirred, circumstances which are comparable to the vitiation studies are given. For this degree of vitiation, by the Equation (3-19) of Mulholland et al. the increase of the CO yields will be 4-fold based on $Y_{CO,wv}$. With the findings of Tsuchiya and Mathieu, assuming flaming combustion, the increase will be less than 2-fold based on $Y_{CO,wv}$.

In this example, the increase of the CO yields is still slight compared to the effect of under-ventilated fires. It represents a situation where, for example, a storage rack is fully on fire and the fuel is partly released into the upper layer. It is not known to what extent the fuel can be released directly into the upper layer with still sustaining a quasi-steady state compartment fire. From detailed studies where the fuel was completely released into a vitiated upper layer, unsteady effects like ghosting flames and extinction are reported (Sugawa et al. 1989, Coutin et al. 2001).

3.2.4 Pyrolysis in the upper layer

In contrast to the results of vitiation studies, significant generation of CO was achieved by pyrolysis of wood that was mounted as lining material in the upper layer. As the pyrolysis process is endothermic, the heat supply was given by a fire source that was located at the bottom of the compartment.

Pitts et al. (1994) conducted natural gas fires between 40 and 600 kW ideal heat release rate in a reduced scale compartment (l * w * h = 1.46 m * 0.98 m * 0.98 m, w_v = 0.81 m, H = 0.48 m), where the ceiling and the upper walls were lined with 6.4 mm Douglas fir plywood for most tests. When the compartment's surfaces were covered with plywood, a significant increase of the CO levels in the upper layer was shown. The increase of the CO

levels correlated with the heat release rates of the gas burner. When the lining material failed and parts of it dropped down and burned in the lower layer, CO levels decreased. The pyrolysis and subsequent combustion of the wood linings led to significantly elevated overall heat release rates compared to the gas burner. The heat release rates also monotonically increased over time until wood burnout was reached. Therefore, the published data cannot be attributed to a constant equivalence ratio. However, by Equation (2-15) the heat release rate to achieve $\Phi = 1$ is found to lie above 400 kW for the compartment. Based on this value a significant increase in the CO concentrations did occur with well-ventilated fires of $\Phi < 0.25$. CO yields are not reported. In his algorithm to predict CO formation (Fig. 2-15) Pitts (1997) considered CO formation from wood pyrolysis only for under-ventilated fires. This disagreement seems to be connected with the above-mentioned (cf. Sect. 2.4.4) square root of 8 error in the determination of the ventilation conditions. Pitts et al. (1994) assumed $\dot{Q}(\phi = 1)$ to be of the order of 200 kW.

Another study on wood pyrolysis in the upper layer was conducted by Lattimer et al. (1998) in their prototype compartment with attached hallway (Fig. 2-10). Sheets of Douglas fir plywood 6.4 mm thick were mounted at the ceiling of the compartment during some tests, which were fuelled by hexane fires as the primary heat source. Only highly under-ventilated fires were achieved. With the GER made up by the overall mass loss rate the CO yields (0.22 g/g at $\Phi = 5.2$ and 0.17 g/g at $\Phi = 5.6$) were shown to be of the order of the level predicted by Equation (2-20). The normalised depletion of O_2 and the normalised yields CO_2 were also in close agreement with the result from the ideal combustion approach (Eq. (2-3)). Only the THC yields were found to be lower than predicted by the ideal combustion approach (Eq. (2-4)) - a fact that could not be fully explained. It was concluded by Lattimer et al. that the GER-concept is able to predict CO, CO_2 and O_2 yields of compartment fires with oxygenated fuels in the upper layer, like wood, cardboard boxes, and fabrics. For upper layer fuels with no oxygen in their chemical structure, it was supposed that these fuels cannot generate additional CO in a hot vitiated upper layer. Instead, upper layer species concentrations might be diluted by added THC. The nominal CO yields would be additionally decreased, as the higher mass loss rates from upper layer fuel increase the denominator for the yield calculation.

From both test series, two conclusions can be drawn with regard to the GER-concept. For over-ventilated fires an additional CO source term from upper layer pyrolysis must be considered at least for unreactive upper layers. Significant wood pyrolysis was reported to start from 280℃ (Pitts et al. 1994), a temperature level that is much too low to expect upper layer oxidation of CO to CO_2. For reactive upper layers ($T_{ul} > 900$ K) it is not known whether CO from upper layer pyrolysis is oxidised such that the GER - CO yield correlation (Eq. (2-20)) would be still valid. For under-ventilated fires the maximum CO yield is almost independent on whether there is upper layer pyrolysis or not.

3.3 Compartment fires with external combustion

As shown by the fire plume properties in the previous sections, increased CO yields from compartment fires are to be expected when the interface height is low and flashover conditions are reached in the room of fire origin. Under these circumstances thermal conditions dominate the gas concentrations with respect to life-threatening conditions. As seen from fatality studies mentioned earlier, many fire victims died in rooms away from the room of fire origin. In order to operate with accurate source terms of CO, the behaviour of CO outside the room of fire origin needs to be considered.

Carbon monoxide concentrations from compartment fires were reported to be frozen out at temperatures below 800 K (Gottuk et al. (1995), cf. Sect. 2.4.3) or 700 K (Pitts (2001), cf. Sect 2.4.4). In between these values lies the minimum temperature increase of 500 K above ambient temperature which was defined by Heskestad (1997) to indicate flaming regions. Newman and Wieczorek (2004) also demonstrated that for unvitiated conditions the CO concentrations along the flame axis were reduced to $X_{CO,wv}$ at the flame tip. This behaviour was used by them as a criterion to define chemical flame heights which were in good accordance with luminous flame heights. From these observations it can be concluded that regions of significant oxidation of CO to CO_2 are associated with flaming.

In their engineering methodology Gottuk and Lattimer (2002) distinguished between two phenomena, namely flame extensions (Fig. 2-11a) and external burning from under-ventilated conditions (Fig. 2-11b), where only the latter phenomenon accounts for the reduction of CO yields. If both phenomena are considered in terms of a compartment fire set-up, flame extensions occur when sufficient heat is released in a compartment with sufficiently *large* opening vents, while external burning from under-ventilated conditions occurs when sufficient fuel is released in a compartment with sufficiently *small* opening vents. Gottuk and Lattimer did not report on differences in the characteristics of the external flames; however, in Fig. 2-11 flame extensions are located at the top of the outflow, while external burning from under-ventilated conditions occurs along the layer interface. To evaluate qualitative differences in the characteristics of both phenomena, the species concentrations along the opening plane are examined.

Wieczorek (2003) presented species mappings from the door vent of his enclosure (Sect. 2.4.7) at different heat release rates and resulting global equivalence ratios. He reported that the species generation in the compartment was not influenced by the hallway which was attached to the compartment during some tests. In Fig. 3-11, the centreline species mappings of the w_V = 0.165 m vent are reproduced from Wieczorek's data. The data of Fig. 3-11a was obtained at 153 kW ideal heat release rate, where 91 kW heat release rate was the minimum rate for flame extensions. The GER of 0.58 represents conditions where

only flame extensions are expected. Fig. 3-11b was recorded at 470 kW ideal heat release rate with Φ = 2.05, which clearly represents conditions where external burning from under-ventilated fires does occur.

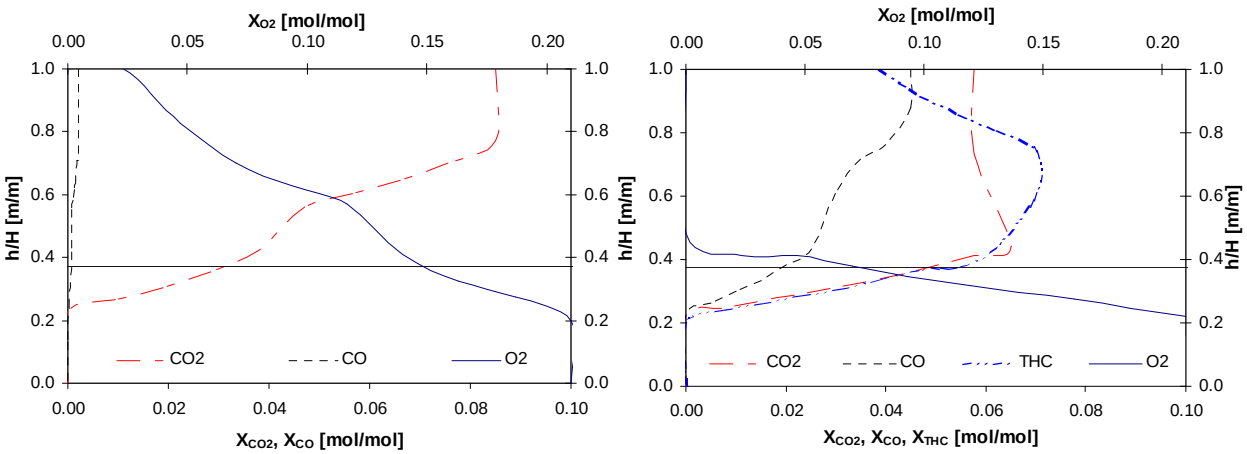

Fig. 3-11a+b. Species concentrations along the centreline of the vent of Wieczorek's test compartment at (a) Φ = 0.58 and (b) Φ = 2.05. The horizontal line indicates the neutral plane height (reproduced from Wieczorek (2003)).

The diagrams illustrate that out-flowing species are not well mixed, contrary to what is commonly assumed for upper layer gases. Instead the species concentrations in the outflow part of the vent resemble a slice through a vertical fire plume which is turned horizontally. The different compositions of the out-flowing gases at Φ = 0.58 and Φ = 2.05 represent fire plume concentrations of different heights in the slices relative to the flame height (cf. Smith and Cox (1992)). The location of the plume centreline is best represented by the greatest fuel concentration or lowest oxygen concentration. The concentrations representing the plume centreline are reached slightly below the soffit for flame extensions. For the strongly under-ventilated case this axis declines, but is still positioned in the upper half of the outflow. From this data it must be assumed that there is a gradual transition between the two phenomena, flame extensions and external burning from under-ventilated conditions. Therefore both phenomena account for the reduction of CO yields by external combustion.

In the following sections first the criteria for external combustion are assessed and extended. Then the efficiency of external combustion to reduce CO yields is examined.

3.3.1 Criteria to assess external combustion

The reasons for investigating external combustion are threefold: firstly to assess the risk of external flame spread to upper floors (conservative risk criteria are those which predict external combustion in the early stages of a fire); secondly to improve the understanding of

fire phenomena and the development of fire models; thirdly to establish the relevance of external combustion within the GER concept.

3.3.1.1 The excess fuel factor and its correlation with the GER

A simple assumption on external combustion is that fuel which is not burned inside the control volume will burn outside. Therefore, assuming that all air entering the compartment is consumed, an excess fuel factor f_{ex} was already defined by Bullen and Thomas (1979) as

$$f_{ex} = 1 - \frac{\dot{m}_{air}}{\dot{m}_f \cdot r_{air}} = 1 - \frac{1}{\phi} \tag{3-21}$$

which can also be expressed by the GER as

$$\phi = \frac{1}{1 - f_{ex}} \tag{3-22}$$

From their own reduced-scale pool fires with liquid and solid fuels they showed that external combustion, “flashover”, occurred when f_{ex} was greater than 0, i.e. the GER was greater than 1. Although this concept is followed in newer studies (Snegirev et al. 2003), in the context of this work it has two shortcomings:

a) The assumption that all air entering the compartment is ideally consumed is not valid for many compartment fires. As can be seen from the oxygen curve of the species mappings above (Fig. 3-11a), the consumption of oxygen is less than ideal. At $\Phi < 1$ the less-than-ideal consumption of air inside the compartment is the precondition for unburned fuel leaving the compartment and hence the precondition for flame extensions.

b) The second assumption that the fuel is ideally burned inside the compartment according the air supply and that all excess fuel is burned outside the compartment makes application of the GER-concept obsolete.

3.3.1.2 The critical mass loss rate and its correlation with the GER

In some studies with wood cribs a critical mass loss rate to obtain external combustion was related to the ventilation factor. When the concept of external combustion at $\Phi = 1$ is expressed by a critical mass loss rate, from Equation (2-15) with $r_{air} = 5.7\ kg_{air}/kg_{wood}$

(Drysdale 1998, p. 331), the critical mass loss rate is calculated as reported from experiments by Kawagoe (1958)

$$\dot{m}_{wood}(\phi = 1) = 0.52 \frac{kg}{s \cdot m^{5/2}} \cdot \frac{1}{5.7 \frac{kg}{kg}} \cdot w_v \cdot H^{3/2} = 0.0912 \frac{kg}{s \cdot m^{5/2}} \cdot w_v \cdot H^{3/2} \quad (3\text{-}23)$$

A study on external combustion was carried out by Hägglund et al. (1974) with wood crib experiments in a 2.9 m * 3.75 m * 2.7 m high concrete compartment with ventilation factors ranging from 0.2 to 2.0 $m^{5/2}$. Flashover was defined by them as external combustion and a temperature under the ceiling exceeding 873 K. It was achieved for ventilation factors starting with 0.89 $m^{5/2}$. They recorded the mass loss rate and found a correlation of the critical mass loss rate with the ventilation factor as

$$\dot{m}_{crit,wood} = 0.05 \frac{kg}{s} + 0.0333 \frac{kg}{s \cdot m^{5/2}} \cdot w_v \cdot H^{3/2} \quad (3\text{-}24)$$

A similar equation was given a few years later by Jansson and Onnermark (1982) from data of a 6.0 m * 3.75 m area compartment made of (lightweight) concrete. The height was not reported. The ventilation factors were altered between 0.9 and 5.1 $m^{5/2}$. Flashover was achieved for ventilation factors above 1.8 $m^{5/2}$. A similar correlation with decreased slope but increased offset value was presented (Fig. 3-12)

$$\dot{m}_{crit,wood} = 0.10 \frac{kg}{s} + 0.02 \frac{kg}{s \cdot m^{5/2}} \cdot w_v \cdot H^{3/2} \quad (3\text{-}25)$$

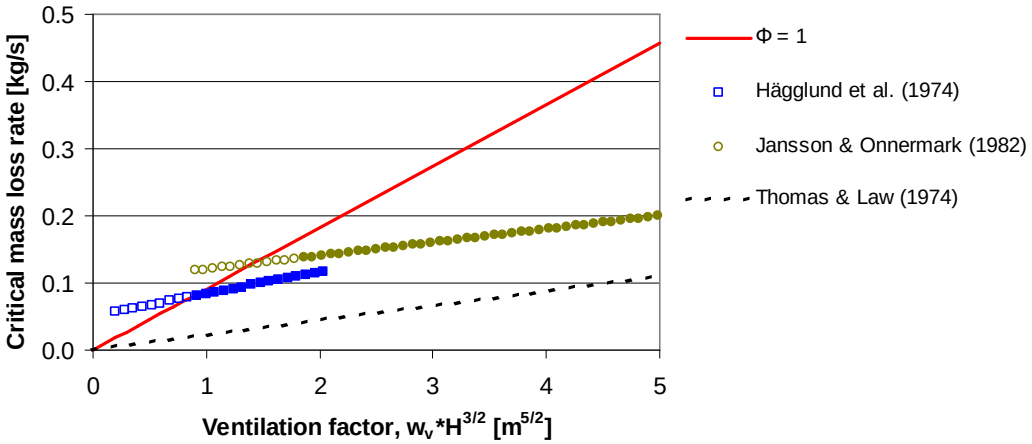

Fig. 3-12. Comparison of reported critical mass loss rates of wood to obtain external combustion. The Φ = 1 line represents the concept of the excess fuel factor. Open dots indicate that the required mass loss rate was not achieved in the tests.

Good agreement with Equation (3-25) was found in a study of Yamada et al. (2002) in a 0.93 m * 0.575 m * 0.375 m high insulated compartment with propane as fuel. To account

for the fuel properties, they calculated the ideal heat of combustion instead of the mass loss rate. They assumed that the mechanism of external combustion is dependent on room temperature which is more influenced by the compartment surface than by the compartment volume (cf. Sect. 3.3.1.3).

Based on several experimental studies, Thomas and Law (1972) correlated the extension of the external plume to the mass loss rate of wood and the vent geometry (Fig. 3-13). They reported

$$\zeta + H = 12.8 \cdot (\dot{m}_{wood} / w_v)^{3/2} \tag{3-26}$$

where ζ is the height of the flame above the window soffit. The beginning of external combustion can be expressed by $\zeta = 0$. Then Equation (3-26) can be reorganised to

$$\dot{m}_{crit,wood} = 0.0218 \frac{kg}{s \cdot m^{5/2}} \cdot w_v \cdot H^{3/2} \tag{3-27}$$

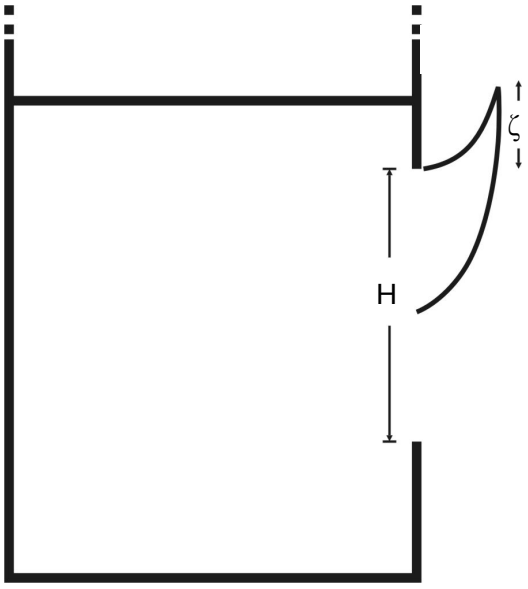

Fig. 3-13. Illustration of the criterion of external combustion by Thomas and Law (1972).

When the critical mass loss rates of the above-mentioned equations are normalised by the mass loss rate to achieve $\Phi = 1$ (Eq. (3-23)), external combustion is expressed in terms of the GER (Fig. 3-14).

Equation (3-24) (Hägglund et al. 1974) becomes

$$\phi_{EC} = \frac{0.55 \ m^{-5/2}}{w_v \cdot H^{3/2}} + 0.37 \tag{3-28}$$

Equation (3-25) (Jansson & Onnermark 1982) becomes

$$\phi_{EC} = \frac{1.1\ m^{-5/2}}{w_v \cdot H^{3/2}} + 0.22 \qquad (3\text{-}29)$$

Since this Equation (3-27) (Thomas and Law 1972) has no offset, it suggests that external combustion occurs at

$$\phi_{EC} = 0.24 \qquad (3\text{-}30)$$

The fact that the equation applies independently of the ventilation factor means it is conservative in the sense of its field of application and that it is acquired from data sets of different compartments. From Equations (3-28) and (3-29) the upper part of Fig. 3-14 with $\Phi > 1$ represents external burning from under-ventilated conditions, while the low Φ values stand for flame extensions. This is consistent with the theory that flame extensions do not occur when the ventilation factor is small relative to the compartment size. It is also consistent with the theory that Equation (3-28) is derived from a smaller compartment than Equation (3-29). However, for both data sets the area of $\Phi > 1$ is an extrapolation and not supported by experimental results of wood fires, as the critical mass loss rates were not reached in the tests due to negative feedback from ventilation effects. Actually an experimental confirmation for the $\Phi > 1$ part of this curve was given by the propane data of Yamada et al. (2003). The impact of reduced ventilation on the mass loss rate especially of cellulosic fuels was discussed in Sect. 3.1.

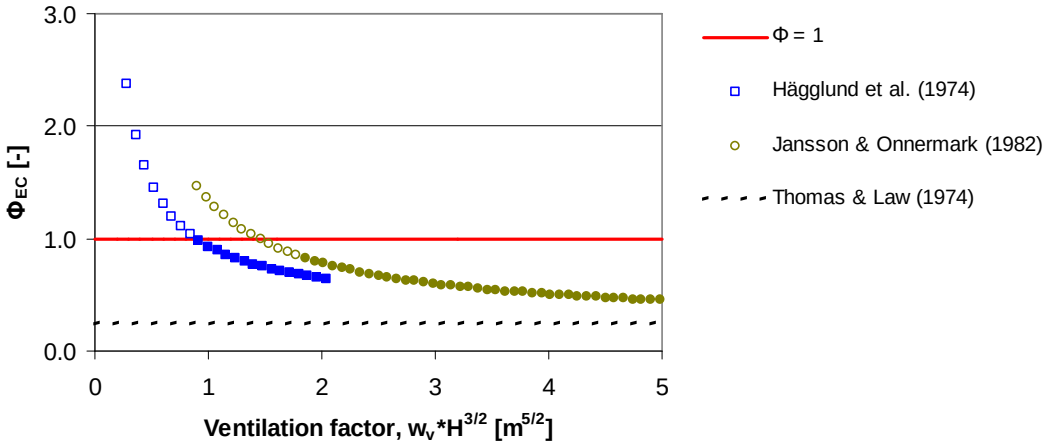

Fig. 3-14. Comparison of calculated GERs to obtain external combustion from the concepts of a critical mass loss rate. The Φ = 1 line represents the concept of the excess fuel factor. Open dots indicate that the required mass loss rate was not achieved in the tests.

It can be concluded that, depending on the geometry of the compartment, external combustion will occur from over-ventilated and under-ventilated fires. In practice, for wood fuelled fires external burning from over-ventilated fires plays the more important role.

3.3.1.3 The ignition index and its correlation with the GER

The criteria mentioned above were developed on a phenomenological basis. An analytical criterion is the ignition index which was introduced by Beyler (1984) (cf. Sect. 2.4.1). When natural combustion is treated as adiabatic all heat released is absorbed by the system. Thus, the lower flammability limit (LFL), as the lowest fuel concentration where the reaction sustains itself, is defined by

$$X_{LFL} = \frac{\int_{T_0}^{T_{AFT,LFL}} n_p \cdot c_p \cdot dT}{\Delta H_C} \tag{3-31}$$

where T_0 is the initial temperature and $T_{AFT,LFL}$ is adiabatic flame temperature (AFT) at the LFL. Coward et al. (1952) showed that lower limits of flammability of gas mixtures can be calculated based on the law of Le Chatelier

$$\sum_{i=1}^{n} \frac{X_i}{X_{LFL,i}} \geq 1 \tag{3-32}$$

where X_i is the mole fraction of a fuel species i in a mixture of fuels and air and $X_{LFL,i}$ is the lower flammability limit of the fuel species i in air alone. If the sum of Equation (3-32) is greater than one, the limit of flammability of the fuel mixture is exceeded. Beyler realised that for most hydrocarbon fuel gases the AFT at the LFL in air is only about 100 K lower than at the stoichiometric limit mixture. He found indications that the AFT at the stoichiometric limit mixture is independent of the diluent and assumed that Equation (3-32) holds at the stoichiometric limit concentration of a fuel mixture. He obtained the ignition criterion he called ignition index (Beyler 1984, 2002)

$$I = \sum_{i=1}^{n} \frac{X_i \cdot \Delta H_{C,i}}{\int_{T_{mix}}^{T_{AFT,SL,i}} n_p \cdot c_p \cdot dT} \tag{2-16}$$

The temperature $T_{AFT,SL}$ lies around 1700 K for most hydrocarbons. Because of the insensitivity of the AFT to the chemical structure and the small differences between the AFT at the lower limit and stoichiometric limit, Beyler assumed that the ignition index is valid for typical C, H and O containing fuels. For fuels containing sulphur, nitrogen or halogen a systematic evaluation of limit temperatures does not exist. For CO and H_2 the $T_{AFT,SL}$ is 1450 K and 1080 K respectively. The equality of the AFT at the lower and upper limit of flammability was shown for these gases (Beyler 2002).

Beyler (1984) also discussed the influence of aerosols, which may contribute as solid or liquid particles. Principally the volatiles which can be evolved from the particles should be

added to the existing gas phase fuels and the heat capacity of the remaining char should be added to the gaseous products. Using the example of propane at Φ = 1.7 with assumed 10 % soot yield based on the carbon content for the upper layer, he showed that the heat capacity of soot is negligible and the fuel volatiles are of marginal interest.

When only one fuel species is present, the ignition index can be expressed on a mass basis by

$$I = \frac{y_f \cdot \Delta H_C}{m_p \cdot c_p \cdot (T_{AFT,SL} - T_{mix})} \geq 1 \tag{3-33}$$

where y_f is the fuel mass fraction in the upper layer and m_p is the ratio of mass of products resulting from burning of a unit mass of upper layer gases. Assuming complete combustion according to Equation (2-4), the fuel mass fraction in an under-ventilated upper layer becomes

$$y_f = \frac{1 - 1/\phi}{1 + r_{air}/\phi} \tag{3-34}$$

Inserting Equation (3-34) into Equation (2-16), expressing the heat of combustion in terms of the ideal oxygen consumption in air using

$$\Delta H_c = \Delta H_{C,O2} \cdot y_{O2}^{\infty} \cdot r_{air} \tag{3-35}$$

and recognizing that

$$m_p = 1 + y_f \cdot r_{air} \tag{3-36}$$

yields

$$\left(\frac{1 - 1/\phi}{1 + 1/r_{air}} \right) \left[\frac{\Delta H_{C,O2} \cdot y_{O2}^{\infty}}{c_p \cdot (T_{AFT,SL} - T_{mix})} \right] \geq 1 \tag{3-37}$$

Assuming a constant heat capacity, the mixing temperature of the stoichiometric mixture of upper layer gases with ambient air becomes

$$T_{mix} = \frac{T_{ul} + y_f \cdot r_{air} \cdot T_a}{1 + y_f \cdot r_{air}} \tag{3-38}$$

Equation (3-37) can be solved for equality conditions. By using semi-universal constants $\Delta H_{C,O2}$ = 13.4 MJ/kg, c_p = 1.1 kJ/(kg*K), $T_{AFT,SL}$ = 1700 K, y_{O2} = 0.233, T_a = 300 K and a typical r_{air} = 14.3, Beyler obtained the relationship between an equivalence ratio Φ_{EC} where

external burning from under-ventilated conditions is achieved and the necessary upper layer temperature T_{ul} (Fig. 3-15). The illustrated correlation is

$$\Phi_{EC} = - 8.135 * 10^{-4}\ K^{-1} * T_{ul} + 2.36 \qquad (3\text{-}39)$$

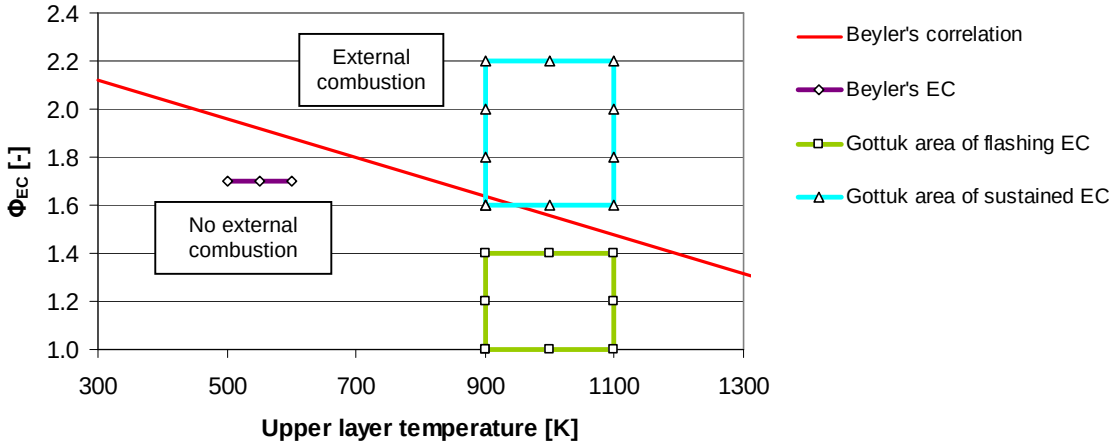

Fig. 3-15. Relationship between the equivalence ratio to achieve external burning from under-ventilated conditions and the necessary upper layer temperature. For comparison the experimental results of Beyler's hood experiment and Gottuk's prototype compartment are illustrated (extended from Beyler (2002)).

The ignition index takes the inerting effects of combustion products inside the compartment into account. Thus, in contrast to the concept of the excess fuel factor where external combustion from under-ventilated conditions starts at $\Phi_{EC} = 1$, from Equation (3-39) Φ_{EC} is greater than one.

When significant amounts of CO and H_2 are present, due to their difference of $T_{AFT,SL}$, r_{air}, and ΔH_C relative to THC, Equation (3-39) loses applicability. On this point Beyler (1984) reported that because of a fortuitous cancellation of errors the equation works reasonably well in most cases.

Beyler (2002) compared the results of Equation (3-39) with experimental data. From his hood experiments (Sect. 2.4.1) he found layer burning away from the plume at $\Phi = 1.7$ for T_{ul} between 500 and 600 K. With Gottuk's prototype compartment (Fig. 2-9) external combustion was first observed in flashes at $\Phi = 1.4 \pm 0.4$ and sustained external combustion occurred at $\Phi = 1.9 \pm 0.3$ for T_{ul} between 900 and 1100 K. These results are illustrated in Fig. 3-15.

3.3.1.4 Extensions of Beyler's external combustion equivalence ratio

Beyler's Φ_{EC} has not yet been compared to experimental data from large-scale compartments. For this comparison the amended GER of "flashover" reported from the TOXFIRE ISO 9705 tests is compared with Beyler's criterion (Fig. 3-16). "Flashover"

represents sustained external combustion (Lönnermark 2006). Although there is much variation in the TOXFIRE data, there is no indication that the data of a specific fuel or specific opening height follows its own significant trend. Hence, for the linear regression, only chlorobenzene (CB6) is excluded because of the known inhibition effects of chlorine. The linear curve fit is

$$\Phi_{EC} = -2.8 * 10^{-3}\ K^{-1} * T_{ul} + 4.634 \qquad \text{for } T_{ul} > 900\ K \qquad (3\text{-}40)$$

The empirical equation from large-scale compartments has a different shape to Beyler's theoretically derived correlation for Φ_{EC}.

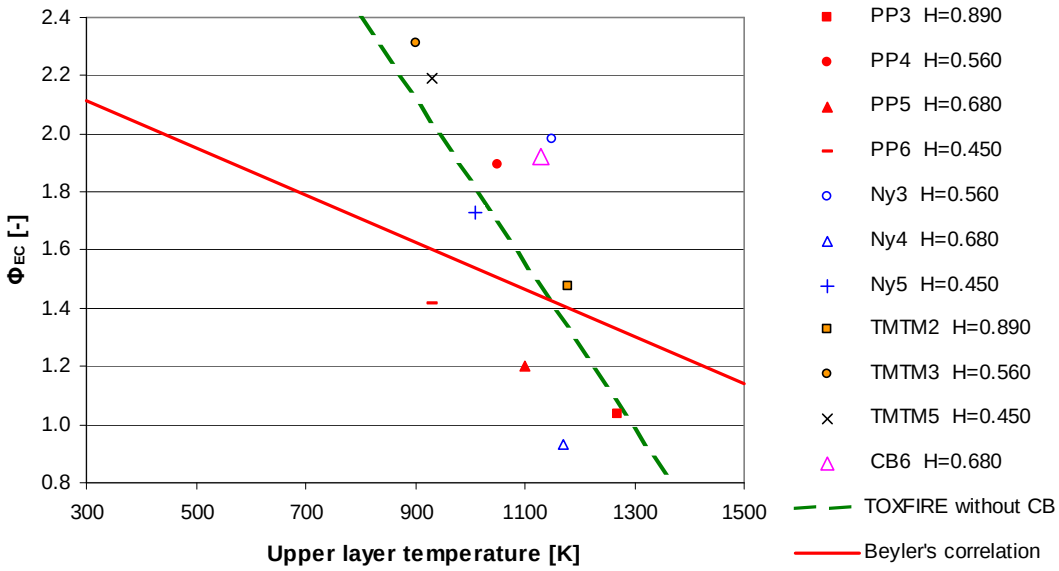

Fig. 3-16. Sustained external combustion at the TOXFIRE ISO 9705 room tests with linear curve fit. Comparison to Beyler's equivalence ratio to achieve external combustion.

The explanation of this behaviour can be found in the fuel properties and the combustion efficiency. With the properties of the TOXFIRE fuels (Tab. 3-2) inserted in Equation (3-37) the solutions for equality conditions lead to a slightly increased Φ_{EC} in the order TMTM, PP, and Ny, especially for the low temperature area (Fig. 3-17).

Table 3-2: Fuel properties assumed by Beyler and for the fuel of the TOXFIRE experiments (Beyler 2002 and Lönnermark and Babrauskas 1996).

	Beyler	PP	Ny	TMTM
$\Delta H_{C,O2}$ [MJ/kg]	13.4	12.67	12.53	13.96
r_{air} [kg/kg]	14.3	14.7	10.02	7.91

The combustion efficiency inside the compartment χ_{comp} and the overall efficiency χ including external combustion also have an influence. Beyler assumed that χ_{comp} behaves

according to the ideal combustion approach (Eq. (2-3)) and that χ becomes 1 if his ignition criterion is fulfilled. However, in large-scale fires real combustion efficiencies are of the order of $0.80 < \chi < 0.95$ (Lönnermark et al. 1996, Blume 2003, p. 83). With additional consideration of the combustion efficiency to be $\chi = 0.85$ for PP the correlation is closer to the experimental data (Fig. 3-17). With respect to the real combustion efficiency Beyler's Φ_{EC} is not always conservative.

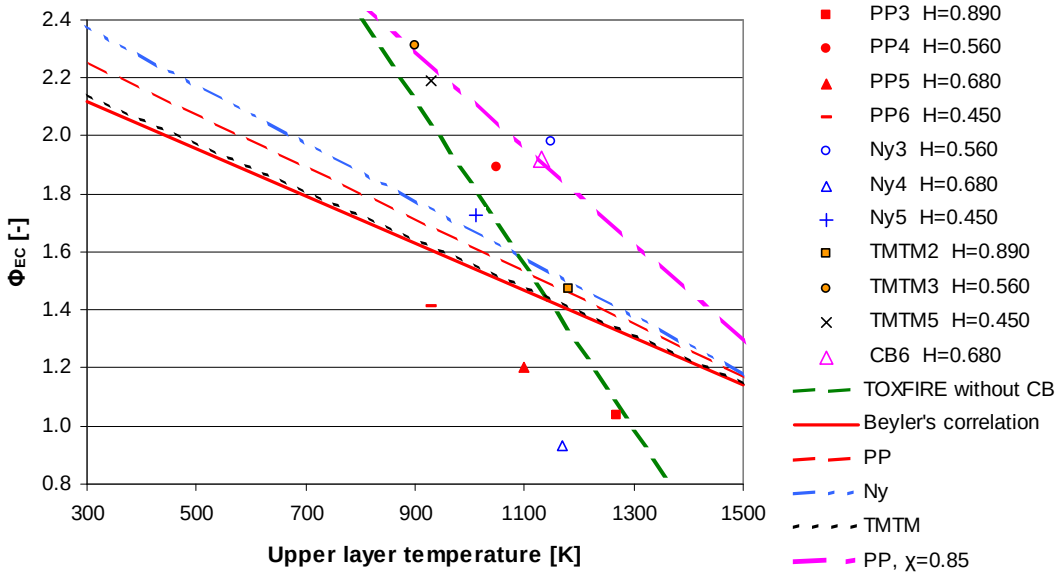

Fig. 3-17. Influence of the fuel properties and the combustion efficiency on Beyler's Equation (3-37) solved for equality conditions. Comparison with the TOXFIRE ISO 9705 room data.

A different set of empirical data can be derived from Morehart's hood experiments with air-addition into the hood gas layer at a distance from the fire plume (cf. Sect. 2.4.2). The reported behaviour of the hood gas temperature after air-addition is reproduced in Fig. 3-18. The initial conditions are represented by the PER (open dots). With the addition of air a significant increase in the hood temperature is taken as a sign of ignition, while an increase of T_{ul} of less than 50 K is interpreted as dilution. Applying this criterion, ignition is considered as starting at $\Phi_{pl} = 1.46$ with $T_{ul} = 505$ K and at $\Phi_{pl} = 1.62$ with $T_{ul} = 530$ K. The other values do not represent the boundary conditions of ignition (Fig. 3-19). This new data is below Beyler's correlation for Φ_{EC} as is the case for Beyler's own hood results. This looks surprising as Beyler's correlation was shown to be non-conservative for the TOXFIRE ISO 9705 room data, especially because the overall combustion efficiency is less than 1. An explanation can be given by looking at the combustion efficiency in two ways. In contrast to the TOXFIRE ISO 9705 room experiments which always achieved upper layer temperatures above 900 K, the hood experiments represent unreactive upper layers where combustion is suppressed by entrainment of upper layer gases. Therefore χ_{comp} is smaller than ideal and the enthalpy of the exhaust gas is higher than assumed from Equation (2-3). An additional contrast to the TOXFIRE data is that short-chained

hydrocarbons like propane and natural gas used for the hood experiments achieve high overall combustion efficiencies, close to 1 (Tewarson 2002).

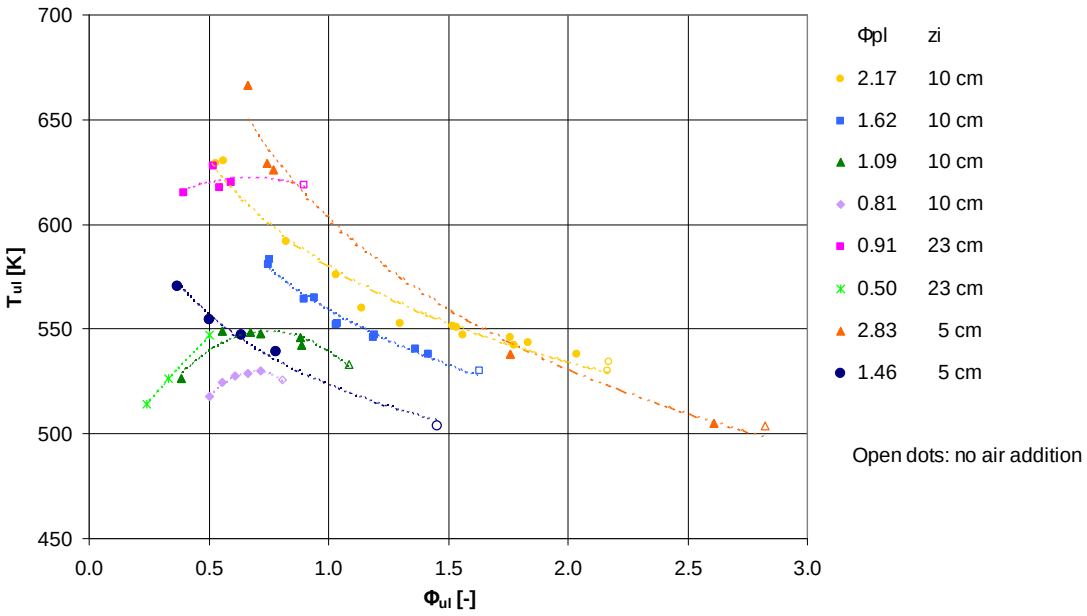

Fig. 3-18. Upper layer temperature and equivalence ratio for initial conditions (open dots) and after air addition (closed dots) during Morehart's hood experiments (reproduced from Zukoski et al. (1991)).

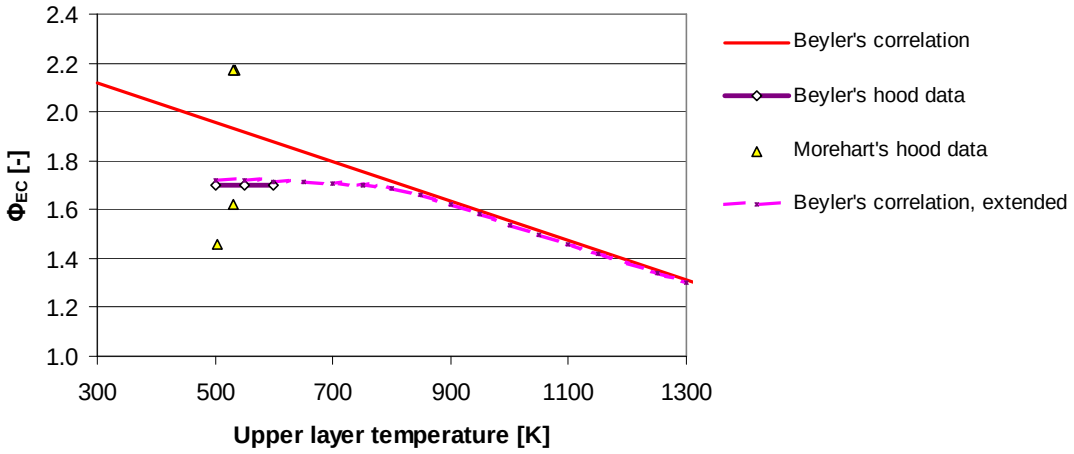

Fig. 3-19. Ignition in hood experiments of Beyler and Morehart in comparison to Beyler's equivalence ratio to achieve external combustion and an extended correlation to account for reduced combustion efficiency within the compartment.

Beyler's correlation for Φ_{EC} (Eq. (3-39)) is derived for an ideal combustion efficiency χ_{comp}. Given that the real combustion efficiency decreases with decreasing temperature, the influence of χ_{comp} must be examined. With soot and intermediate species neglected, Equation (3-34) extended for χ_{comp} becomes

$$y_f = \frac{1-\chi_{comp}/\phi}{1+r_{air}/\phi} \tag{3-41}$$

Equation (3-35) does not need to be extended, because it refers to combustion outside the control volume. Equations (3-36) and (3-38) have to be used with y_f expressed by Equation (3-34), because the stoichiometric mixture related to the equivalence ratio does not change. Equation (3-37) becomes

$$\left(\frac{1-\chi_{comp}/\phi}{1+1/r_{air}}\right)\left[\frac{\Delta H_{C,O2}\cdot y_{O2}^{\infty}}{c_p\cdot(T_{AFT,SL}-T_{mix})}\right]\geq 1 \qquad (3\text{-}42)$$

Systematic data on the temperature dependency of combustion efficiency was calculated from of Zukoski et al. (1991) hood experiment data (Fig. 3-9). The data can be approximated by

$$\chi_{comp} = 0.4036\ \ln(T_{hood}) - 1.7069 \quad \text{for} \quad 500\ K < T_{hood} < 850\ K \qquad (3\text{-}43a)$$

and

$$\chi_{comp} = 1 \qquad \text{for} \quad T_{hood} > 850\ K \qquad (3\text{-}43b)$$

With Equation (3-43) inserted in Equation (3-42) the numerical solution for equality conditions is illustrated in Fig. 3-19 for the available temperature range.

The calculated equivalence ratio to achieve external burning from under-ventilated conditions never exceeds $\Phi_{EC} = 1.72$. The new approach helps to explain why in hood experiments ignition occurred earlier than predicted by Beyler's correlation for Φ_{EC}. Besides low upper layer temperatures another reason for a reduced χ_{comp} is incomplete mixing within a compartment, which has two effects: firstly, χ_{comp} is lower than ideal, and secondly the fuel concentration is higher than average at the top end of the exhaust vent (cf. Fig. 3-11).

Flame extensions do not occur in hood experiments but they might have happened during the TOXFIRE ISO 9705 room experiments, when the data is found below Beyler's correlation at high upper layer temperatures (Fig. 3-16). Although validation data does not exist, the concept of the ignition index in principle does not exclude the occurrence of flame extensions. During flame extensions the combustion efficiency within the compartment is also smaller than ideal and instead of T_{ul} the reference temperature must be taken from flaming zones. Both factors decrease the equivalence ratio to allow for external combustion.

The ignition index and the derived extended correlations for Φ_{EC} are analytical tools for the prediction of external combustion. For the still rare validation data they proved to be of reasonable applicability. Consistent validation data over a temperature range from unreactive to reactive upper layers is lacking and flame extensions are difficult to cover by

the concept. Therefore the combined influence of the combustion efficiency within the compartment and the overall combustion efficiency could not be studied by a single set of data.

3.3.1.5 Conclusions about the criteria to assess external combustion

Different phenomenological and analytical criteria have been reviewed to assess external combustion. For the purpose of this work it is useful that these criteria can be correlated with the GER. The excess fuel factor is of no help with regard to the GER-concept. The approach by critical mass loss rates depends on the compartment geometry and hence is not suitable for general application. The transition between the two phenomena of external combustion for a single data set and the range of results between different data sets are illustrated (Fig. 3-14) by the correlation of the mass loss rates with the GER.

Beyler's analytical ignition index is more generally applicable. The rare validation data can each be explained by consistent extensions of Beyler's original correlation for an equivalence ratio to achieve external combustion. The inclusion of flame extensions is more difficult in practice because they relate to compartment fire kinetics which is not considered in the ignition index. An overall tool for the prediction of external combustion, that accounts to the multifaceted phenomena in compartment fires, has not yet been developed.

The application of flame height correlations to predict flame extensions is of very limited help because the flame is typically located in both compartment layers where its shape is influenced by inflow and outflow, which bend the flame away and towards the opening vent. For the controlled conditions of Wieczorek's (2003) compartment, flame extensions were shown to be strongly dependent on the vent width, a parameter that is not covered by any flame height or ceiling jet correlation. Instead the flame shape influenced by the flow field can be studied by numerical fire simulation with a CFD model (Chapter 4).

According to the GER-concept CO yields undergo an important change between $0.5 < \Phi < 1.5$. External combustion was shown to occur in an extended range, between $\Phi_{EC} \approx 0.3$ and $\Phi_{EC} \approx 2.3$. Therefore in many cases the final CO yields are considerably influenced by the occurrence and efficiency of external combustion.

3.3.2 Efficiency of external combustion to reduce CO yields

The efficiency of external combustion depends mainly on the oxygen supply of the secondary flames which is a function of the ventilation/vitiation conditions of the secondary control volume and the entrainment into the reacting areas.

In typical buildings and structures, three main types of secondary control volumes can be distinguished:

a) The movement of fire gases into the channels of smoke extraction systems where the gas mixture is cooled down without significant additional air supply. These circumstances do not lead to a notable decrease of the CO yields.

b) In contrast the release of fire gases into the ambient atmosphere significantly decreases CO, which is treated in detail.

c) The most important and complex situation is external combustion in an attached hallway which fills up with fire gases. This is also treated in detail.

3.3.2.1 CO reduction in ambient atmospheres

Gottuk et al. (1992) reported on hexane fuelled experiments in their prototype compartment with different window vent sizes (Fig. 2-9). They showed that CO yields were reduced to about 10 % of the compartment yields, i.e. to about 0.02 g/g, when sustained external combustion occurred. This happened at $\Phi > 1.8$. For lower equivalence ratios $\Phi \approx 1.1$ CO yields just under 0.2 g/g were obtained at the vent and at the duct. Gottuk et al. reported that the “flashing” or “bursting” modes of external combustion between $0.9 < \Phi < 1.8$ were quite ineffective. One explanation suggested was that a potentially ignitable mixture is not ignited because a source of ignition was lacking at the vent.

Because of the difficulties with opening vent measurements described above, the TOXFIRE ISO 9705 room experiments do not provide data for a direct comparison of species yields at both locations (Sect. 2.4.5). Therefore a comparison can only be made of CO yields at $\Phi < \Phi_{EC}$ with CO yields at $\Phi > \Phi_{EC}$. In Fig. 3-20 the normalised CO yields at the duct are given. The GER of external combustion is also indicated for each experiment. A significant decrease of the normalised CO yields happened for the TMTM experiments as well as for CB6. For PP3, PP5, and PP6 as well as for Ny4 there is actually an increase in the CO yields, although “flashover” was reported. The comparison with Fig. 3-16 shows that the data points of these experiments are located at the lower end of the T_{ul} to Φ correlation and are excluded by the proposed extension of Beyler’s correlation. This result is consistent with Gottuk et al. (1992), that external combustion is not simply a question of

'yes or no'. The more the ignition criterion is fulfilled, the more effective the reduction of CO becomes.

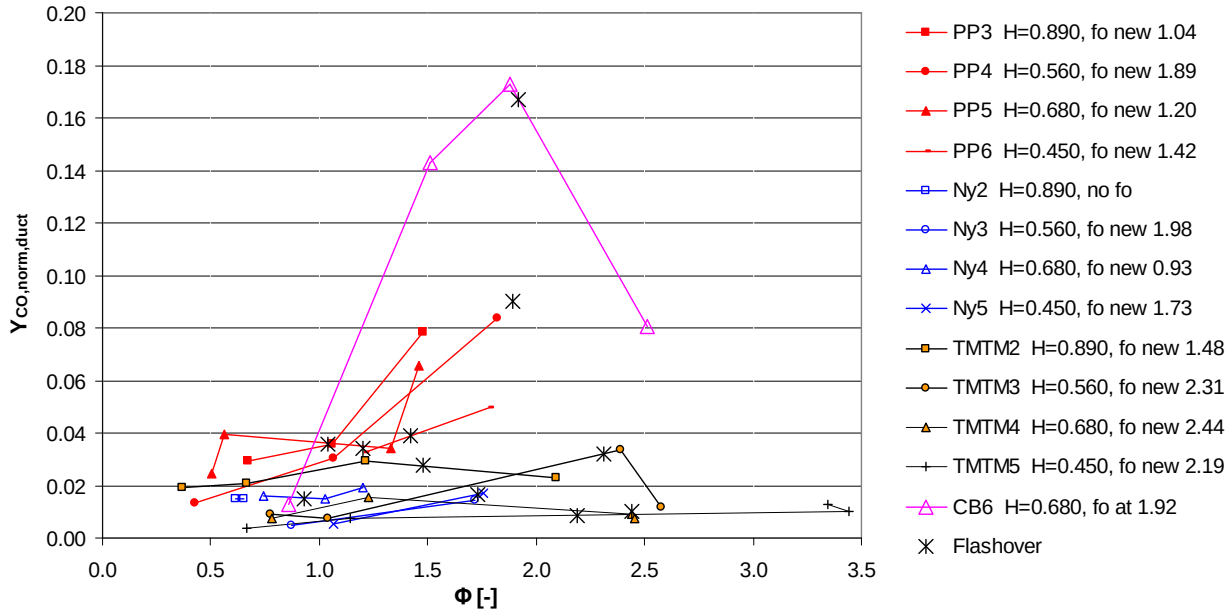

Fig. 3-20. Normalised CO yields at the duct correlated with the amended GER. The GER of external combustion "flashover" is also indicated. Calculated from TOXFIRE ISO 9705 room data given by Lönnermark et al. (1996).

3.3.2.2 CO reduction in adjacent hallways

The conditions for CO reduction in adjacent hallways are less ideal than in ambient air because the secondary fire plume is attached to the ceiling or the wall and entrains less air than under open conditions. Additionally the hallway might fill up with fire gases, resulting in depleted oxygen concentration. The two available studies on CO reduction in adjacent hallways were presented by Gottuk and Lattimer (cf. Sect. 2.4.3) and by Wieczorek (cf. Sect. 2.4.7).

In their engineering methodology Gottuk and Lattimer (2002) advised considering the effects of external combustion only when the exhaust gases leave the compartment to flow into fresh air below the hallway's smoke layer (cf. Fig. 2-13). This is quantified in terms of the relative smoke layer depth $\gamma = \delta/z_l$. This approach lacks any reference to the actual composition of the atmosphere in the attached hallway. Although there is no validation data, calculation of Beyler's ignition index should enable the significance of external combustion in adjacent spaces to be more accurately assessed. Beyler's Equation (3-37) can be used with variable oxygen mass fraction y_{O2} to account for vitiated conditions in an hallway. The decrease in the ignition index is illustrated in Fig. 3-21a for two GERs and two compartment upper layer temperatures. On the other hand vitiation in the hallway occurs together with elevated temperatures in the hallway upper layer. These increase the

mixing temperature of the stoichiometric mixture and hence increase the ignition criterion (Fig. 3-21b). Simple analysis of Beyler's ignition criterion shows that a depletion of the oxygen content of one mass percent is compensated by a temperature increase between 105 K and 130 K depending on the exact equivalence ratios and initial level of oxygen mass fraction. When the secondary fire plume is completely immersed in the vitiated upper layer of the hallway the conditions are comparable to those described in Sect. 3.2.3.3 for phenomenon (b). From the vitiation studies it must be expected that the oxidation of high amounts of CO to CO_2 is less effective than under unvitiated conditions. These theoretical considerations are also backed up by Lattimer et al. (2005) from experiments in the prototype compartment with different window vent areas to the adjacent hallway. In the case of a relative smoke layer depth $\gamma > 1$ they reported a continuous increase of the final CO yields until a value about $Y_{CO} = 0.23$ g/g was reached (Fig. 3-22). This value is close to the maximum yields, ignoring the effects of external combustion (Fig. 2-14).

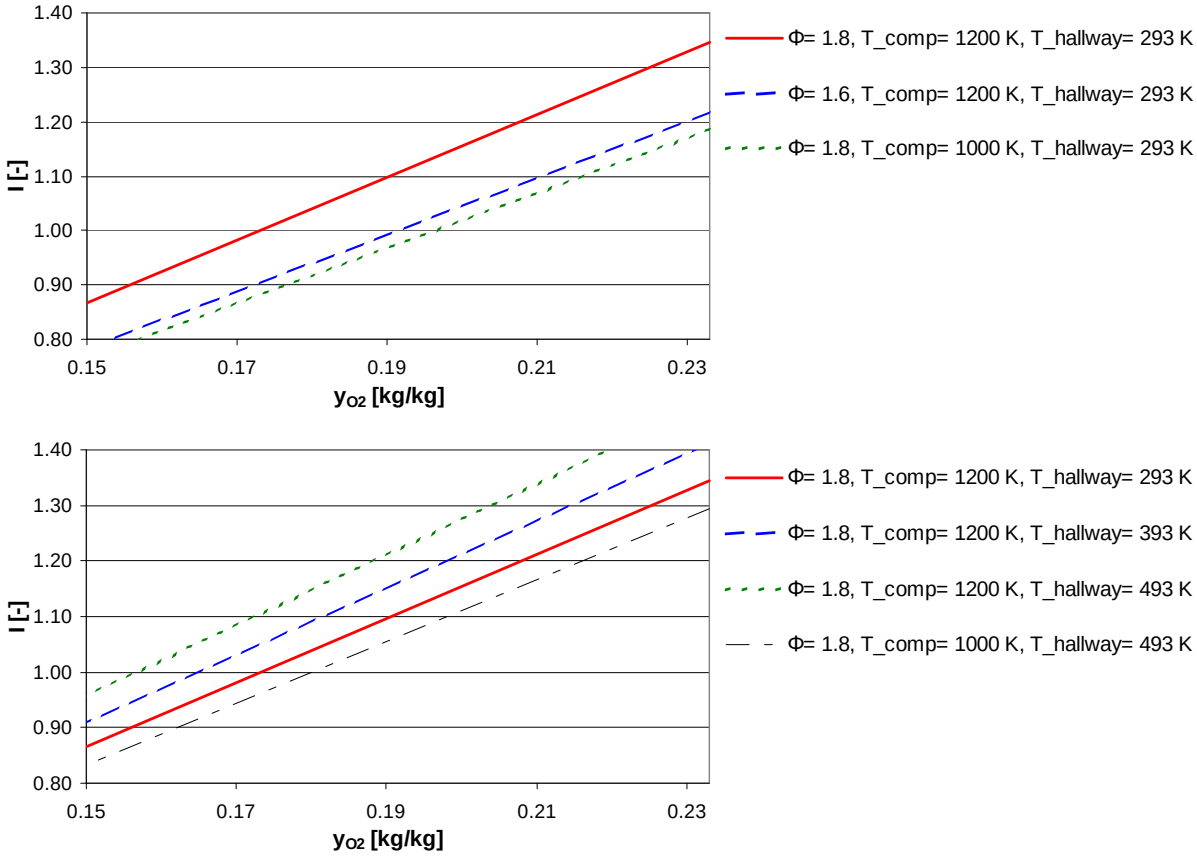

Fig. 3-21a+b. Influence of the hallway oxygen mass fraction on the ignition index. Basic curve with $\Phi = 1.8$, $T_{comp} = 1200$ K, and $T_{hallway} = 293$ K. Variation of (a) Φ and T_{comp} and (b) $T_{hallway}$ and T_{comp}.

Gottuk and Lattimer's prototype compartment is capable of producing fires with high equivalence ratios where the secondary plume entrains much of the hallway mixture into the upper layer. Due to the separated air inlet of the compartment, the ventilation conditions of compartment and hallway were independent.

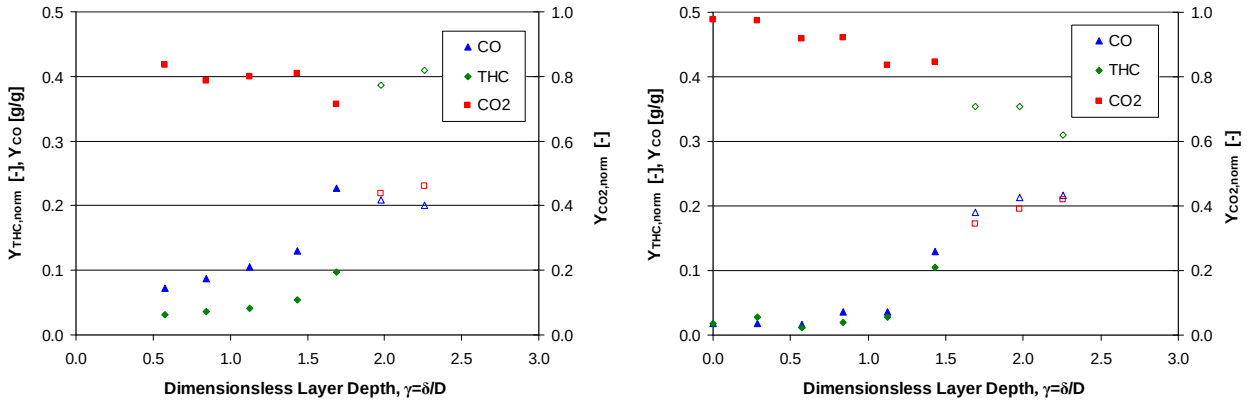

Fig. 3-22a+b. Influence of the relative upper layer height on the final species yields of strongly under-ventilated fires (Φ = 2.8). Open dots represent experiments without external combustion. CO species yields are higher for the (a) larger (0.08 m²) window vent than for the (b) 0.04 m² window vent. The maximum yields both are on the same level as described for a single compartment with no account taken of external combustion (reproduced from Lattimer et al. (2005)).

A more realistic situation for structural fires was given for Wieczorek's "hallway study" with the door vent between compartment and hallway (Sect. 2.4.7.2). As only flame extensions were achieved in this study, relatively few air was entrained from the lower layer to the upper layer of the hallway. Hence, for the quasi-steady state conditions tested the compartment equivalence ratio Φ_{comp} was only slightly higher than the equivalence ratio of the complete construction Φ_{all}. Although the data set is small the efficiency of CO reduction can be expressed by the ratio of the CO yields at the hallway-to-ambient plane to the CO yields at the compartment-to-hallway plane. From Fig. 3-23 it can be seen that this ratio correlates with the difference in the equivalence ratio of the two control volumes, i. e. with the additional ventilation in the hallway. When no extra ventilation is given for the hallway ($\Phi_{comp} - \Phi_{all} = 0$), the ratio $Y_{CO,hallway} / Y_{CO,comp}$ remains unchanged under ideal conditions. For $\Phi_{comp} - \Phi_{all} \approx 0.2$, based on the small amount of data available, roughly 50 % of the compartment CO is reduced.

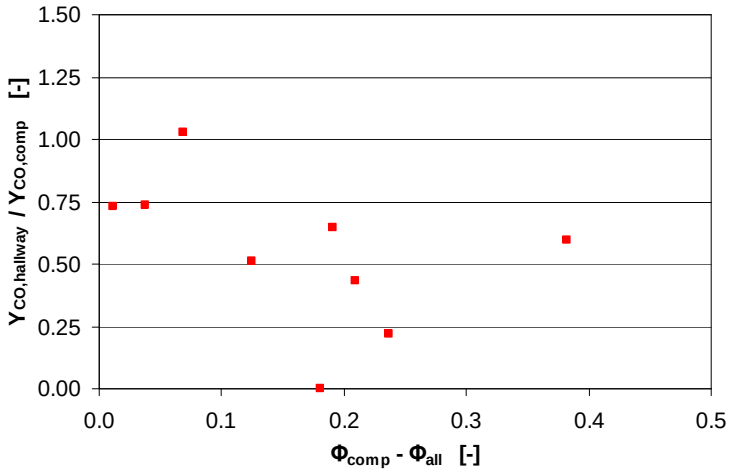

Fig. 3-23. Efficiency of CO reduction by flame extensions in correlation with the additional ventilation of the hallway compared to the compartment (calculated from data of Wieczorek (2003)).

4 APPLICABILITY OF NUMERICAL FIRE SIMULATION

In this chapter the extent to which state-of-the-art numerical fire simulation provides functional simulation results for an assessment of species yields in compartment fires is examined. The state-of-the-art of fire modelling is represented by computational fluid dynamics (CFD) models. These models, which are also called field models in the fire protection community, provide solutions for the basic conservation equations of fluid flow, reaction and heat transfer. One of the main distinctions between different modelling approaches concerns turbulence modelling. Conventionally, Reynolds-averaged Navier-Stokes (RANS) models are used, which include sub-models for turbulence such as the k-ε model, which is most frequently used. In this model two additional partial differential equations are used for the turbulent kinetic energy of the turbulence k and the energy dissipation rate ε. Another new approach to turbulence modelling is by Large Eddy Simulation (LES), where large-scale motions are resolved directly, while small-scale motions are modelled or ignored (Cox and Kumar 2002, Novozhilov 2001).

To capture the details of the chemical reaction zone in a fire, characteristic mesh sizes below 1 mm would be required (Cox and Kumar 2002). For fire protection applications, where domain dimensions of several metres are typical, simplifications have to be made. A common simplification is the assumption of a one-step, complete and irreversible reaction between fuel and oxygen with the reaction velocity controlled by mixing rather than by chemical kinetics (Novozhilov 2001).

4.1 Main features of the Fire Dynamics Simulator

The model used is the “Fire Dynamics Simulator” in the current version 4 (FDS4), developed by the NIST (McGrattan 2006a) and widely used for fire safety engineering purposes. In FDS4 turbulence is treated by means of the Smagorinsky form of Large Eddy Simulation.

The combustion model in FDS4 is based on the assumption that combustion is mixing-controlled. With this model all species of interest are described in terms of a mixture fraction Z(x, t). The mixture fraction is a conserved quantity representing the fraction of material at a given point that originated in the fuel stream. Z is defined as

$$Z = \frac{r_{O2} \cdot y_f - (y_{O2} - y_{O2}^{\infty})}{r_{O2} + y_{O2}^{\infty}}; \quad r_{O2} = \frac{\nu_{O2} \cdot M_{O2}}{\nu_f \cdot M_f} \tag{4-1}$$

It varies from Z = 0 where the oxygen mass fraction y_{O2} is y_{O2}^{∞} = 0.233 to a value of Z = 1 indicating a zone of only fuel. M_f and M_{O2} are the fuel and oxygen molar weights

respectively and ν is the stoichiometric coefficient. The relations between the mass fraction of each species and the mixture fraction Z are called “state relations” (Fig. 4-1). With the mixture fraction all mass fractions of fuel, N_2, O_2 and combustion products (CO_2, H_2O and a fixed amount of CO and soot chosen by the user) are coupled. Fuel and oxygen cannot coexist in one cell. A characteristic, fuel-dependent value of Z is the stoichiometric value Z_{st}. The location of the “flame sheet” which represents the flame as a two dimensional surface embedded in a three dimensional space is characterised by $Z(x, t) = Z_{st}$. The state relation for the oxygen mass fraction provides the information to calculate the local oxygen mass consumption rate. The local heat release rate is calculated from the local oxygen consumption rate at the flame surface multiplied by the fuel dependent heat of combustion per unit mass of oxygen $\Delta H_{C,O2}$.

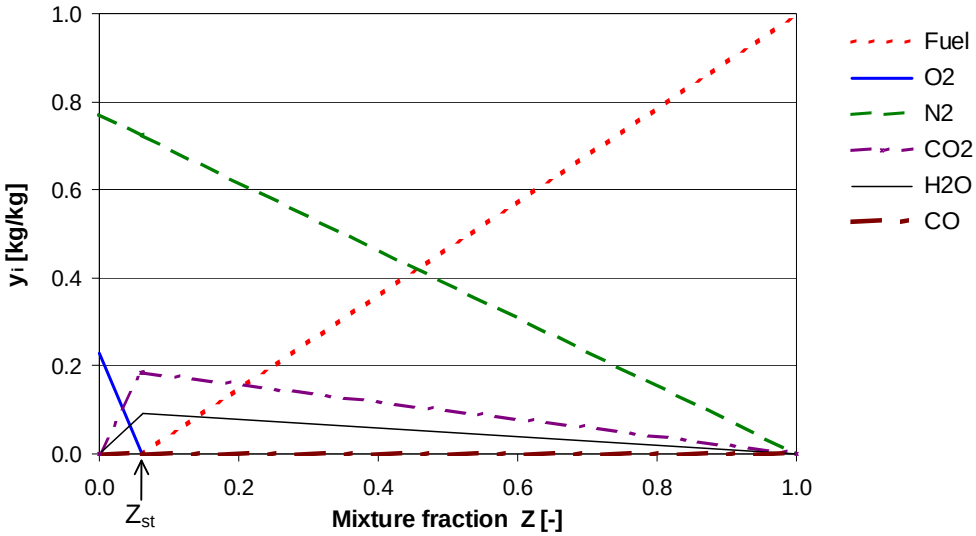

Fig. 4-1. State relations for hexane with CO_2, H_2O and CO and as combustion products. The stoichiometric value Z_{st} locates the highest level of combustion products. y_{CO} are typically close to 0.

The model has some enhancements for coarse grids. On coarse grids the local mixing rate of fuel and oxygen is over-predicted, leading to elevated heat release rates at the base of the burner. To compensate for this, the value Z_{st} where the flame sheet is predicted might be shifted to the lower value $Z_{st,eff}$ defined by

$$Z_{st,eff} = Z_{st} \cdot \min\left(1, C \cdot \frac{D^*}{\delta x}\right) \tag{4-2}$$

where C is an empirical constant equal to 0.6 and δx is the nominal size of a grid cell. The non-dimensional characteristic fire diameter D* is given (McGrattan 2006a) in the common definition

$$D^* = \left(\frac{\dot{Q}}{\rho_\infty \cdot c_p \cdot T_\infty \cdot \sqrt{g}} \right)^{2/5} \tag{4-3}$$

D* can also be estimated based on local values of the mixture fraction near the burner. This concept provides a reasonable prediction of the flame height (McGrattan et al. 2003), however in flashed-over compartments with bad burner resolution (i.e. $Z_{st,eff} < Z_{st}$) the concept is not fully verified (McGrattan 2006b).

A second enhancement of the combustion model is implemented to prevent too much energy from being released too close to the burner when a coarse grid is used. Thus an upper boundary is imposed on the local heat release rate per unit area of flame sheet. This upper boundary is calculated from the assumption that the simulated flame sheet area will always exceed the area of a cone

$$A_{cone} = \pi \cdot r_f \sqrt{r_f^{\,2} + z_{fl}^{\,2}} \tag{4-4}$$

where r_f represents the radius of the fuel bed and z_{fl} is the flame height calculated by Heskestad's Equation (3-11). When the simulated surface area is only slightly larger than A_{cone}, the upper boundary estimate will prevent too much energy from being released too close to the fuel bed. The local excess energy which exceeds the upper boundary is redistributed over the entire flame volume. For well-resolved fires the upper boundary does not interfere with the simulation (McGrattan 2006a).

The third enhancement of the combustion model is a suppression criterion. For oxygen concentrations smaller than a certain temperature-dependent limiting oxygen concentration $X_{O2,LL}(T)$ the heat release is only simulated at sufficient temperature (Fig. 4-2). The curve is defined by the limiting oxygen concentration $X_{O2,LL}$ (default: $X_{O2,LL}(T = 273\ K) = 0.15$) and the critical flame temperature T_{crit} (default: $T_{crit}(X_{O2} = 0) =$

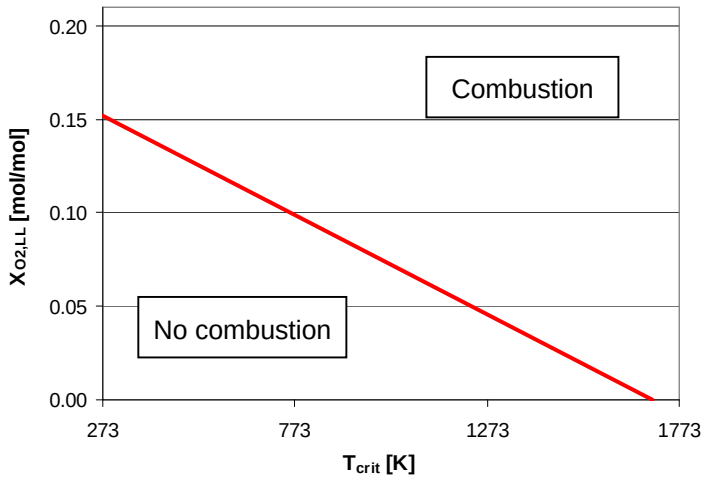

Fig. 4-2. Default setting of the suppression criterion of FDS4 (McGrattan 2006a).

1700 K). When the criterion applies, e.g. for vitiated conditions, fuel and oxygen are assumed to coexist in one grid cell and the values for Z are no longer valid. Although it looks similar, the suppression criterion should not be confused with the equivalence ratio Φ_{EC} (Fig. 3-15) since the concentration of inert combustion products is not taken into account. Instead, for any mixture which contains a fraction of fuel, i.e. $Z > Z_{st}$ or $Z > Z_{st,eff}$ respectively, combustion is simulated when the mixture meets fresh air. Hence, for certain conditions FDS4 is known to over-predict the extent of reacting zones (McGrattan 2005).

4.2 Validation studies

Since FDS is probably the most frequently used CFD-model in the fire protection community, many validation studies have been performed. Some of these are referenced in the FDS Technical Reference Guide (McGrattan 2006a). Within the scope of this work the focus of validation is on

- temperature prediction of under-ventilated fires,
- mass flows, and
- the prediction of reacting zones, i.e. flame heights and external combustion.

4.2.1 Literature review

A study of the flow patterns of doorway flows was given by McGrattan et al. (1998) by comparison of FDS1 simulation results with the experiments of Steckler et al. (1982, 1984). The simulation results agree very reasonably with the experimental data.

Major changes to the combustion model were implemented in FDS2 (McGrattan et al. 2003). From FDS2 to FDS4 the main modifications of the combustion model to the form described above were the alteration of the fixed empirical constant C from 0.025 to 0.6 (Equation (4-2)) and different default values for the suppression criterion (Fig. 4-2).

An extensive comparison of the plume characteristics (flame height, entrainment number, centreline temperatures) predicted by plume equations (cf. Fig. 3-6) and FDS2 is given by Ma and Quintiere (2003). They found the flame height to be reasonably well predicted in comparison with Zukoski's equations. The best results were reported for a grid resolution of $\delta x = 0.05$ m. Temperatures at the flame tip and entrainment numbers were found to be close to empirical estimates.

A recent study with FDS3 simulation results compared to gasoline test fires in a room similar to the ISO 9705 room is given by Zou and Chow (2005). They reported that temperature and radiative heat flux were in good agreement with experimental results, even when the flames occupied most of the room volume. The temperatures predicted near the ceiling agreed within 10 % deviation during the fire growth state. For the peak heat release rate of about 2.6 MW, where the measured temperatures exceeded 700℃, the temperatures were under-predicted by FDS3 by about 100℃. Although the study was reported to be on a post-flashover fire in terms of upper layer temperatures exceeding 600℃ and flames coming out of the door vent, the G ER calculated by Equation (2-15) with $\Delta H_{C,O2}$ = 12.68 MJ/kg (pentane, (SFPE 2002)) was less than $\Phi \approx 0.75$.

In a study by Floyd et al. (2001) propane fires in Wieczorek's half-scale ISO 9705 compartment (Sect. 2.4.7) were simulated with an early version of FDS2. The paper refers to experiments with the 0.33 m wide door-like vent with steady state heat release rates of 90 kW, 270 kW and 440 kW. The comparison showed reasonable agreement for the 90 kW fire but displayed an increasing over-prediction of the simulated temperatures for increased heat release rates, with temperatures in the lower layer over-predicted by a factor of about 2. The authors concluded that for the "well-ventilated" (90 kW), "moderately-ventilated" (270 kW) and "highly under-ventilated" (440 kW) fires the performance of FDS deteriorated; however the results were mostly still acceptable. The degree of under-ventilation was not mentioned in that paper. Later Wieczorek (2003) reported for the same compartment configuration with about 420 kW heat release rate an equivalence ratio of $\Phi = 1.0$. This suggests an equivalence ratio of only $\Phi = 1.05$ for the "highly under-ventilated fire".

4.2.2 Own studies

4.2.2.1 Fully developed fires in the half-scale and full-scale ISO 9705 compartment

The same experiments in Wieczorek's compartment which were used in validation studies by Floyd et al. (2001) are simulated for the author's own validation of FDS4. The domain was discretised by a grid resolution of $\delta x = 0.05$ m for the compartment and $\delta x = 0.02$ m for the vent area. The scenario was simulated with the heat release rates given by Floyd et al. until steady state was achieved. In Fig. 4-3 the temperatures of the front corner rake reported for the experiments and the simulations with FDS2 (Floyd et al. 2001, Floyd 2006) are compared with the author's own results. For heat release rates of 90 kW and 270 kW the new results were in good agreement with the experimental data concerning the temperature level and the location of the interface height. The S-shape of the temperature curve over the elevation was not so well predicted by Floyd et al. However, in

both simulation studies the upper layer temperatures at 270 kW were already somewhat over-predicted. For 400 kW ($\Phi \approx 1$) upper layer temperatures were considerably over-predicted in both simulation studies. Again the lower layer temperatures were predicted better with FDS4 than with FDS2. When the ideal heat release rate of the FDS4 simulation was further increased, the compartment temperatures also increased but no experimental data is given.

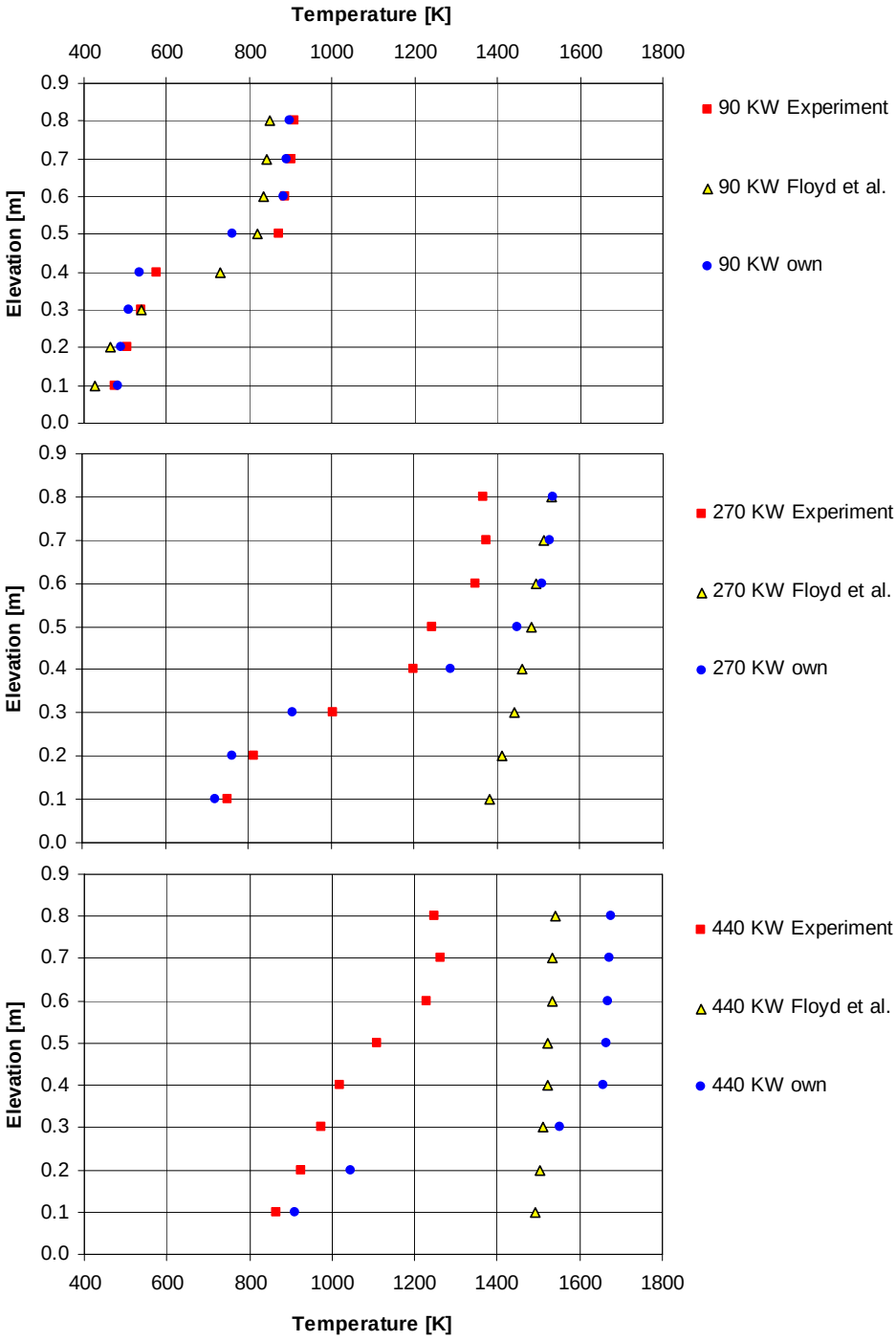

Fig. 4-3a-c. Comparison of temperatures in Wieczorek's compartment (Sect. 2.4.7) with 0.330 m doorway and different heat release rates. Experimental data and simulation results with FDS2 (Floyd et al. (2001), Floyd (2006)) and the author's own simulations with FDS4.

Vent flows were also studied based on the results with Wieczorek's compartment. With the same domain resolution of $\delta x = 0.05$ m for the compartment and $\delta x = 0.02$ m for the vent area, different vent widths like those described by Wieczorek (2003) (cf. Sect. 2.4.7) were simulated until steady states were reached. The simulated air inflows (Fig. 4-4, open dots, sometimes overlaid) showed reasonable agreement with the reported mass flows (closed dots) and good agreement with the Kawagoe-Equation (2-15). Different dots for one ventilation factor represent different ideal heat release rates. For $w_V = 0.660$ m the fires were over-ventilated (cf. Fig. 2-32). The small values for simulated mass flows for this vent size are obviously due to low simulated temperatures for the given heat release rates. The experimental temperature values were not given.

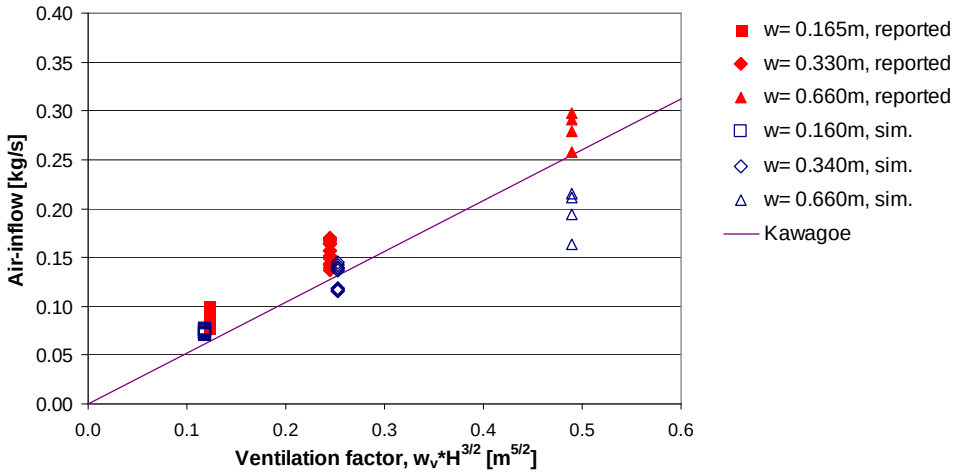

Fig. 4-4. Comparison of air-inflows in Wieczorek's experiments (Sect. 2.4.7) that were reported (closed dots), simulated by FDS4 (open dots) and calculated with Equation (2-15) (line).

The TOXFIRE experiments in the ISO 9705 room were also simulated with $\delta x = 0.05$ m resolution with prescribed mass loss rate. The suppression criterion was switched off. Upper layer temperatures from the experiment and the simulation were averaged from the readings of the upper five thermocouples 0.10 m to 0.70 m below the ceiling (Lönnermark 2006). Using the example of the polypropene series it can be seen that these temperatures (Fig. 4-5a) are well predicted for well-ventilated fires. For $\Phi > 0.5$ the reported values (closed dots) were always much higher than the simulated temperatures (open dots). For under-ventilated fires, in contrast to the results shown before, the simulated temperatures always significantly decrease. The mass flows (Fig. 4-5b) were also predicted well for well-ventilated fires. For under-ventilated fires they decrease significantly below the expected value. This decrease is consistent with the decrease of the simulated temperatures.

As shown in Fig. 2-38 by the experimental results in the ISO 9705 room and by Drysdale (1998, p. 333), the compartment temperatures reach a maximum at $\Phi \approx 1$ and slightly

decrease with the increased degree of under-ventilation. In post-flashover fires, the vent flows have always been shown to be quite independent of the compartment temperatures and the ventilation conditions (cf. Fig. 2-2).

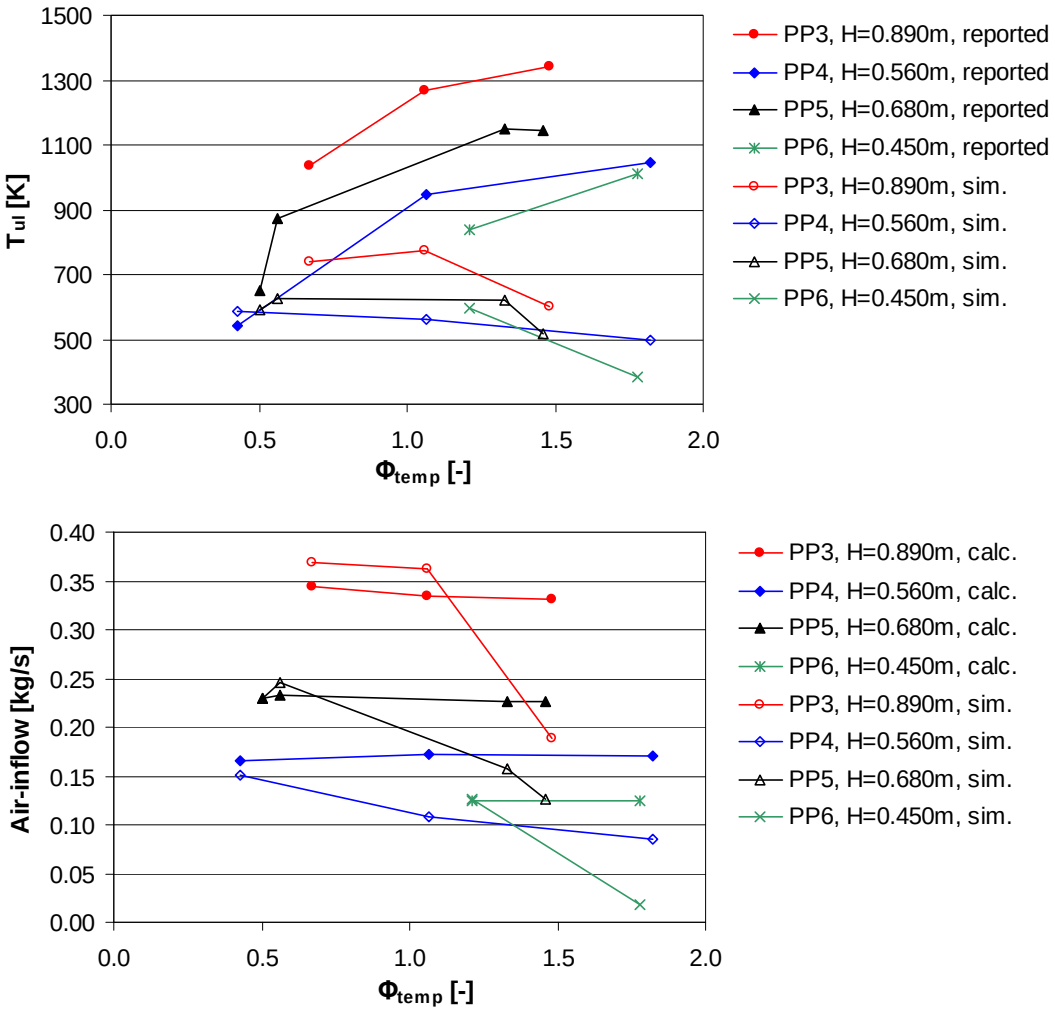

Fig. 4-5a+b. Comparison of (a) upper layer temperatures and (b) air-inflows of the TOXFIRE ISO 9705 experiments (closed dots) and simulation by FDS4 (open dots). Experimental air-inflows and the GER are amended (cf. Sect. 2.4.5.2).

The FDS4 simulation results from Wieczorek's compartment and the full-scale ISO 9705 compartment were both in reasonable accordance with the experimental data for well-ventilated conditions. For an equivalence ratio exceeding approximately 0.5, the upper layer temperatures in the half-scale compartment exceeded the experimental values. The performance of FDS4 further deteriorated with increasing heat release rates. In contrast, simulated temperatures from the full-scale ISO 9705 compartment achieved the maximum levels for over-ventilated fires. Then the temperatures rapidly decreased together with the mass flows. This was accompanied by a drastic decrease of the heat release rate in the compartment. Similar results such as those from the simulations of the TOXFIRE experiments were obtained from simulation of the iBMB ISO 9705 room experiments.

Both types of behaviour were known to the code developer (McGrattan 2006b), but a definite explanation could not be given. The deterioration starts when the location of the flame sheet moves from above the fuel bed for over-ventilated fires to the vent for under-ventilated fires (Fig. 4-6a+b). For the half-scale experiments a large amount of heat is still released inside the compartment (Fig. 4-6b). For the full-scale compartment at different discretisations the flames were in all cases strongly suppressed. One of the principal differences of the experimental results from the half-scale and large-scale compartment was that Wieczorek reported flame extensions at equivalence ratios below 0.35 (notably, for the smallest width, a rather artificial form of external combustion occurred (cf. Sect. 3.1)). In contrast, no external combustion was reported by any full-scale ISO 9705 experiment at $\Phi < 0.7$. From this, the different behaviour in under-ventilated fires is believed to be related to the enhancements of the FDS4 combustion model (Sect. 4.1), which are tuned for pre-flashover conditions. In particular the upper boundary of the local heat release rate per unit area of the flame sheet, which is imposed by the assumption of the flame sheet to be a cone-like shape (cf. Eq. (4-4)), could be an impediment in some cases. It seems reasonable to assume that in under-ventilated conditions the area of the interface layer between over-stoichiometric and under-stoichiometric mixture, i.e. the flame sheet area, depends on the vent geometry and inflow situation. When these only allow for a small flame sheet area with under-ventilated conditions, the upper boundary of the local heat release rate per unit area will prevent the mixing-equivalent heat release rate from being released inside the compartment.

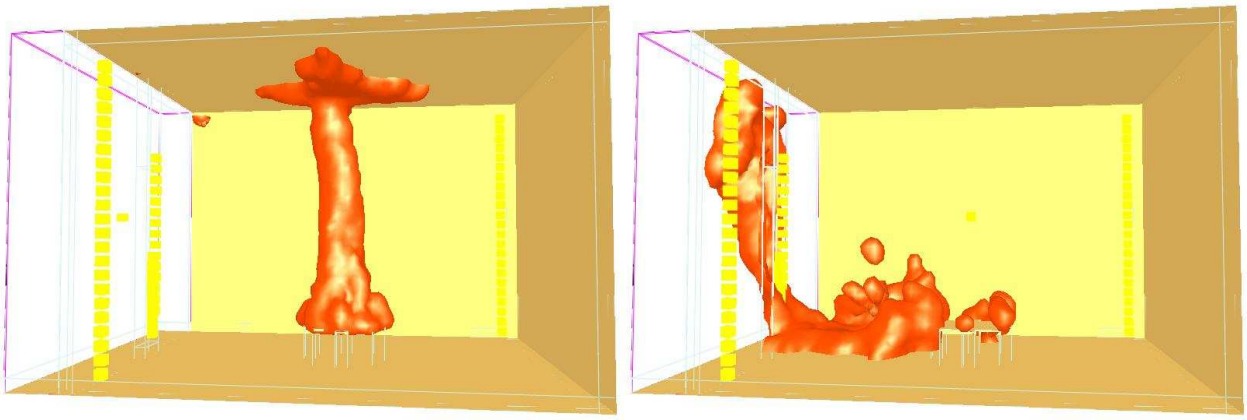

Fig. 4-6a+b. Screenshots of different locations of the flame sheet from simulated experiments of Wieczorek. Plume (a) for well-ventilated fires and (b) flame sheet along the interface between inflow and outflow and external combustion for under-ventilated fires.

4.2.2.2 Flame heights and flame extensions

Validation work was also done on flame height predictions for open plumes and the prediction of flame extensions. To examine the influence of the grid resolution, open fire

plumes were simulated with resolutions of $\delta x = 0.025$ m, $\delta x = 0.050$ m, and $\delta x = 0.010$ m. The fire source was given by a 0.20 m * 0.20 m propane gas burner with linearly increasing heat release rate $0 < \dot{Q}^* < 10$ to represent most kinds of accidental fires. As in real flames the simulated flame height fluctuated (cf. Sect. 3.2.2.1). The simulated instantaneous flame height was taken as the elevation where 99 % of the prescribed heat release rate was released. The fluctuating values were averaged for the mean flame height z_{fl}. In Fig. 4-7 the simulation results are compared with appropriate empirical plume equations of Cox and Chitty (Eqs. (3-9) and (3-10) respectively) for $\dot{Q}^* < 0.55$ and of Heskestad (Eq. (3-11)) for $\dot{Q}^* > 0.12$ (cf. Fig. 3-6). Each grid resolution is represented by a symbol. A closed symbol is given when, due to a relatively coarse grid, FDS shifted the stoichiometric mixture fraction Z_{st} to $Z_{st,eff}$. This is indicated by a fire resolution index (FRI) smaller than 1 (cf. Eq. (4-2)). The flame height is generally under-predicted for $\dot{Q}^* < 0.4$. Unfortunately but not unexpectedly, a grid dependence is observed, whereby coarse grids lead to lower flame heights. The use of $Z_{st,eff}$ is of little influence for the given cases. For the $\dot{Q}^* > 1.0$ area, the simulated flame heights are in reasonable agreement with Heskestad's equation.

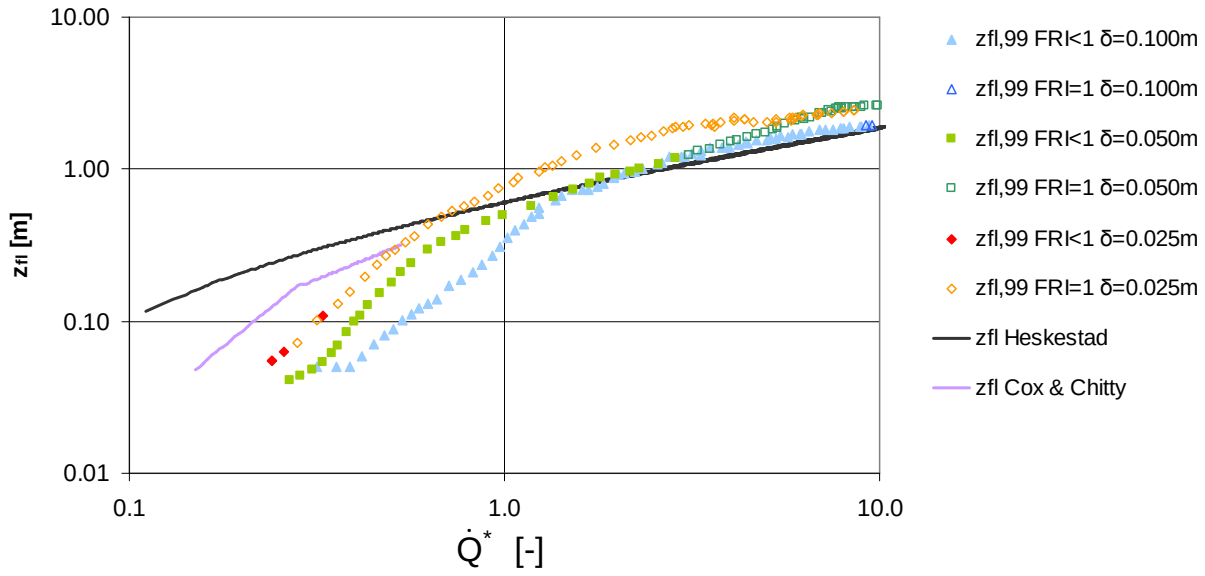

Fig. 4-7. Simulated mean flame heights for different grid resolutions in comparison with Equations (3-9) and (3-10) (Cox & Chitty 1985) and Equation (3-11) (Heskestad 1983).

With plume height correlations (Sect. 3.2.2.2) or criteria to assess external combustion (Sect. 3.3.1.5) the prediction of flame extensions is nearly impossible, because these do not take into account the exact compartment geometry and the flow field from a compartment fire. Therefore the occurrence of flame extensions in Wieczorek's compartment is simulated and compared with experimental results. Wieczorek reported flame extensions at different ideal heat release rates for different vent widths (Tab. 4-1). For the $w_V = 0.660$ m vent only a range of the heat release rate is known.

Table 4-1. Reported ideal heat release rates where flame extensions started (data from Wieczorek (2003), p. 145).

Width [m]	HRR_{id} [kW]	Φ [-]
0.165	91	0.32
0.330	127	0.26
0.660	107 - 203	0.13 - 0.24

Wieczorek's compartment was simulated with different vent sizes with a $\delta x = 0.050$ m and a $\delta x = 0.025$ m resolution. For the coarse resolution the original vent height H = 0.825 m was discretised as H = 0.800 m instead of the exact value. In two additional simulations this was compensated by an extended width. Wieczorek reported heat release rates allowing for flame extensions based on observations. In the simulations the heat release rates were increased until the chosen criterion was fulfilled, that 0.3 % of the heat release rate had to be burned outside the compartment. The simulation results (Fig. 4-8) were in all cases above the observed values, but the experimental curve is essentially captured by the simulation results. A significant grid resolution dependence was not observed. It can be concluded that FDS4 is suitable for studying flame extensions in over-ventilated compartments with simple geometry.

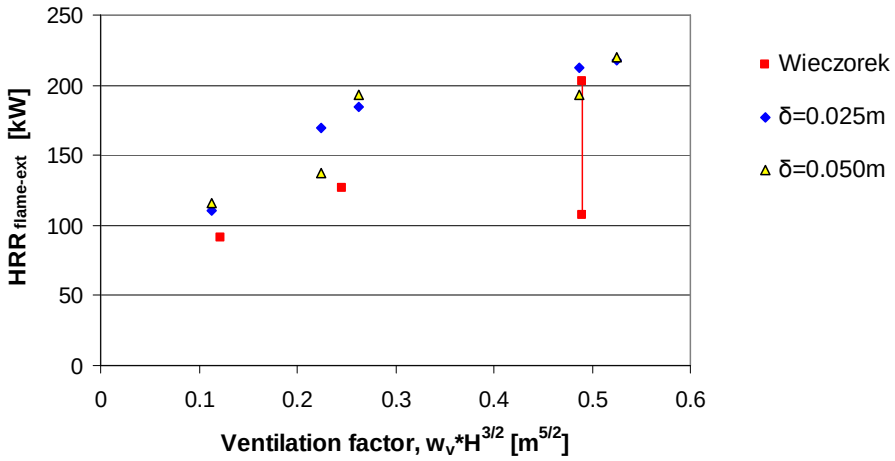

Fig. 4-8. Comparison of observed and simulated heat release rates to allow for flame extensions in Wieczorek's compartment.

4.3 Relationships between mixture fraction, equivalence ratio and ignition index

The studies mentioned above dealt with features which are within the designated modelling capabilities of FDS4. For the scope of this work the prediction of external burning from under-ventilated conditions is also of interest. These phenomena exceed the

capabilities of the current combustion model. Under the assumption that the ignition index is principally suited to predict the reactivity of a mixture (cf. Sect. 3.3.1.3), the relationships between the main parameters mixture fraction Z, equivalence ratio Φ, and ignition index I are explained. These parameters can be illustrated by a ternary diagram.

4.3.1 Illustration by the ternary diagram

The FDS4 combustion model works with mass fractions of fuel, air, and coupled final combustion products. These variables can be illustrated by a ternary diagram (Fig. 4-9). In the diagram, the fuel mass fraction and the air mass fraction are each shown by one axis (instead of air, oxygen can be chosen, but the oxygen content never exceeds 0.23). The third axis depicts the content of inert species in the mixture. These are the fractions of coupled final combustion products (CO_2, H_2O, CO, and soot) and additional nitrogen from depleted oxygen in air. At any location within the triangle or at its edge, the sum of the fractions of air, fuel and inerts is 1.

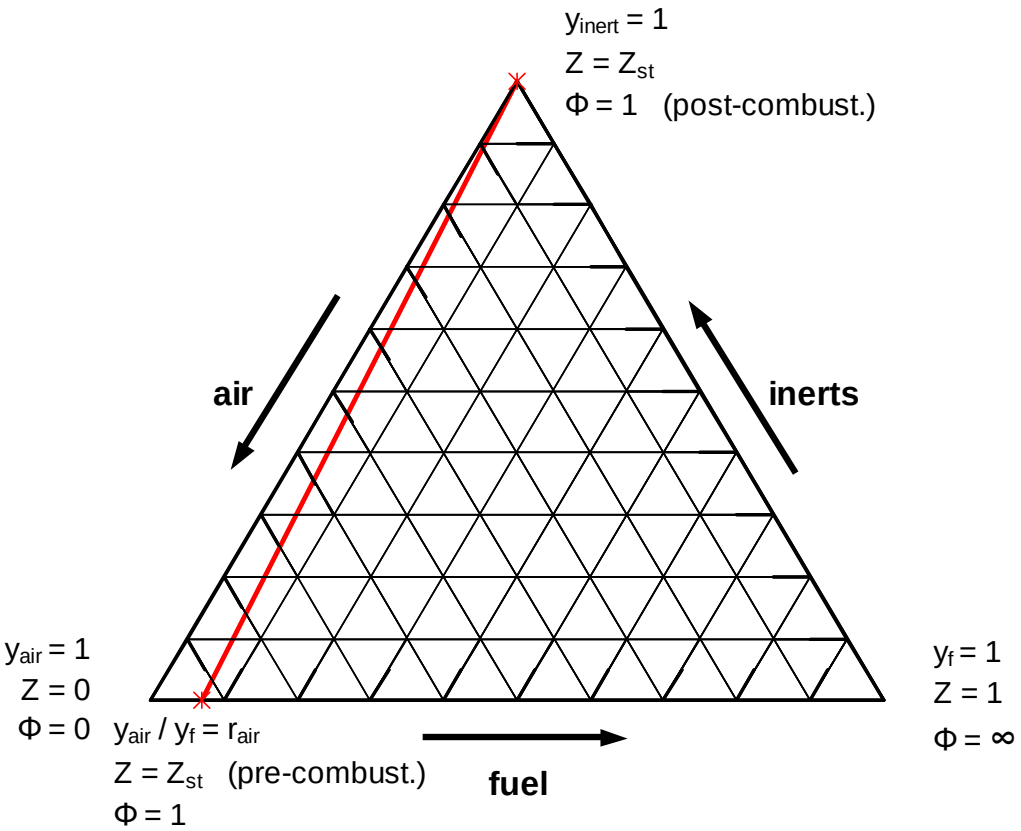

Fig. 4-9. Ternary diagram of a reacting system of a typical hydrocarbon (r_{air} = 14.3) in air. The characteristic values at the vertices of the triangle are given together with the line of stoichiometric combustion which connects the y_{inert} = 1 vertex with the $y_{air} / y_f = r_{air}$ point (by example of typical r_{air} = 14.3).

As the state relations from the mixture fraction Z (Fig. 4-1) refer only to post-combustion conditions, the mixtures expressed by Z are located on the $y_f = 0$ and $y_{air} = 0$ axis of the

triangle. The characteristic values Z = 0, Z = Z_{st}, and Z = 1 are located at the vertices of the triangle (Fig. 4-9). The equivalence ratio in its basic definition (Equation (2-1)) describes pre-combustion conditions, which can be expressed on the y_{inert} = 0 axis of the triangle. Combustion of a stoichiometric mixture (y_{air} / y_f = r_{air}) changes the system along the connection line between Φ = 1 and Z = Z_{st}. The ignition index is also calculated for a stoichiometric mixture which is located on this line. From any point in the diagram, mixing with air takes place along a line directed to the y_{air} = 1 vertex.

Beyler's ignition index is defined for the stoichiometric mixture of fuel-rich exhaust gases with ambient air (cf. Sect. 3.3.1.3). By assumption of ideal combustion, the process of combustion, mixing and possibly external combustion is illustrated in the ternary diagram (Fig. 4-10). An un-combusted mixture of Φ = 1.7 with typical r_{air} = 14.3 is represented by point ①. Ideal combustion shifts the mixture in parallel to the line of stoichiometric combustion to point ②. Mixing with ambient gas will dilute the mixture along the line directed to the y_{air} = 1 vertex. The ignition index is calculated for the intersection of this line with the stoichiometric combustion line (point ③). The value of the ignition index is temperature-dependent (cf. Fig. 3-15). In the case of external combustion, the mixture is combusted along the line of stoichiometric combustion, until point ④ is reached for ideal conditions. If no combustion is achieved, the mixture is further diluted by air until point ⑤ is reached in pure air.

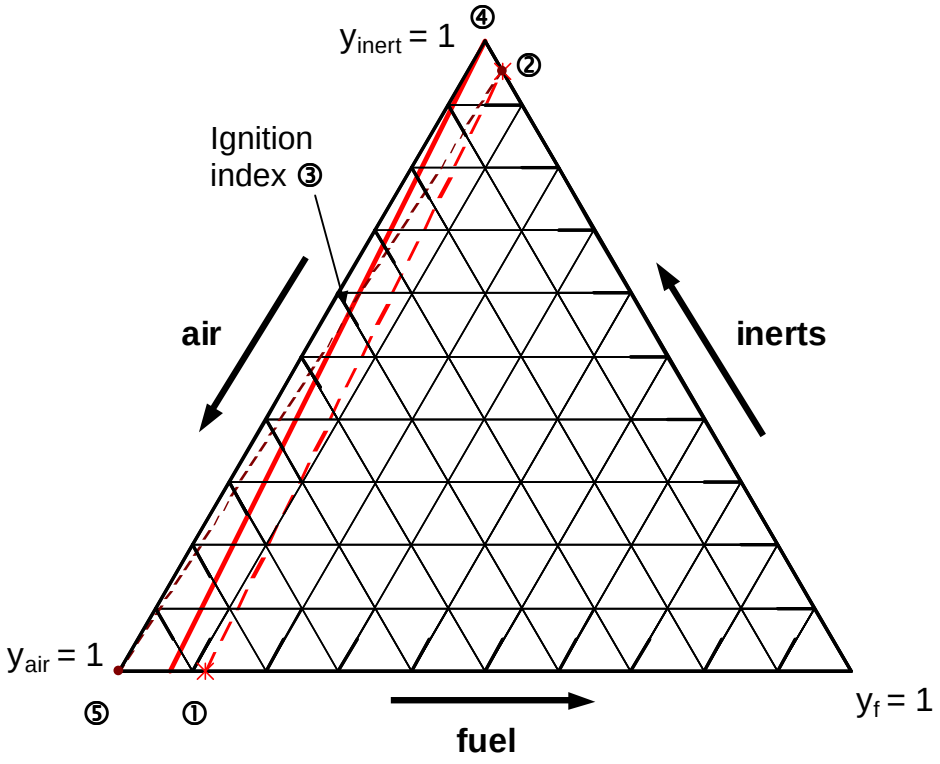

Fig. 4-10. Ternary diagram of a typical hydrocarbon (r_{air} = 14.3) in air. The mixture starts un-combusted at Φ = 1.7 (①), is ideally combusted to a fuel-rich mixture (②), diluted with ambient air to stoichiometric mixture (③), and either externally combusted (④) in case of T_{ex} sufficient to obtain I ≥ 1, or further diluted with air until point (⑤).

4.3.2 Suitability of the FDS4 suppression algorithm for assessing external combustion

In FDS4 the mixing process of fuel-rich exhaust gases and air (Fig. 4-10 between points ② and ③) cannot be simulated, because the mixture fraction is only defined for the two edges of the diagram where fuel and oxygen do not coexist. Hence, in the simulation the system changes along the edge of the triangle. The possible mixture fractions of the grid cells adjacent to the fuel-rich cells are located on the $y_f = 0$ axis (Fig. 4-11). The default setting of the suppression criterion (cf. Fig. 4-2) is indicated on this axis. The default oxygen concentration of $X_{O2} = 0.15$ for T = 273 K represents $y_{air} = 0.71$ (fuel: hexane). The mixture fraction and temperature of the grid cells adjacent to the fuel-rich cells are queried by the suppression criterion of the FDS4 combustion model. A grid dependence of the suppression criterion is given when the actual oxygen concentration gradient (mixture fraction gradient respectively) is the same: in a fine mesh, the oxygen-concentration in a cell next to the cell where the flame sheet is located is smaller than for a coarse mesh. Therefore fine meshes trigger the suppression criterion earlier than coarse meshes. From the figure it can also be seen that external combustion in unvitiated air creates a large gradient that is not covered by the setting of the suppression criterion. Increasing the value for $X_{O2,LL}$ over 0.15 is no solution, because combustion inside the compartment will be suppressed.

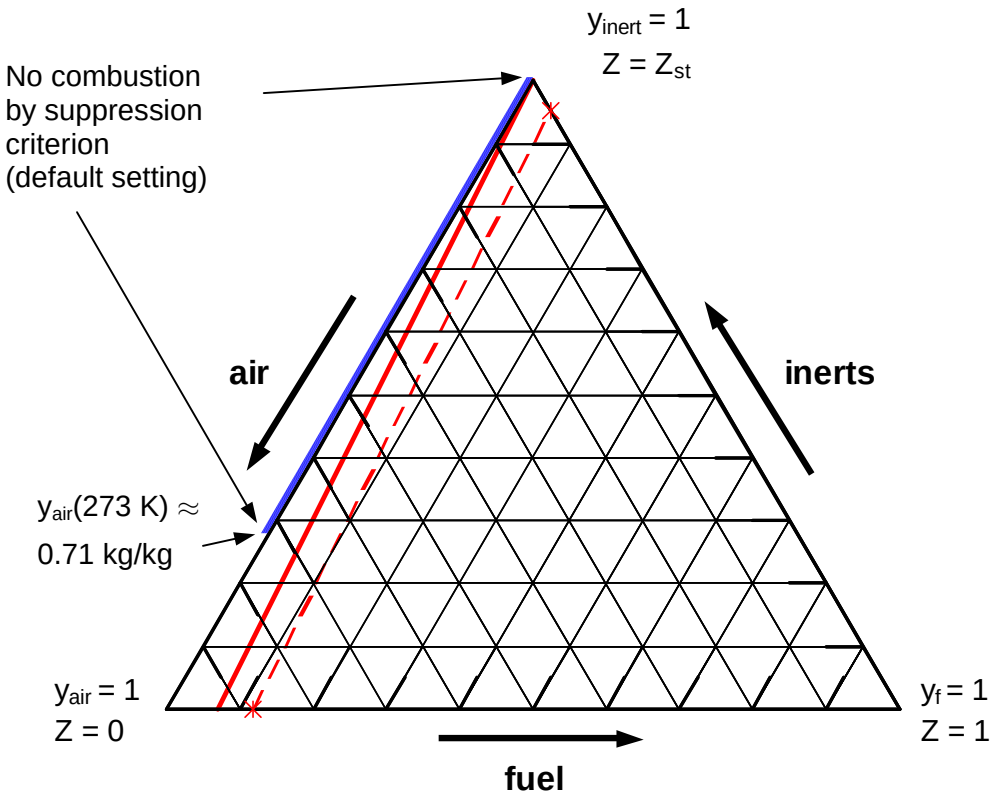

Fig. 4-11. Illustration of the suppression criterion that refers to the properties of the grid cells adjacent to the flame sheet.

4.3.3 Combining FDS4 output data with Beyler's ignition criterion

To overcome the limits of the FDS4 combustion model, Beyler's (extended) ignition criterion (Sect. 3.3.1.3 and 3.3.1.4) can be post-processed from the properties of the exhaust gases. To account for local conditions, the relationship must be given between the mixture fraction Z and the local equivalence ratio Φ_{loc} that is used as the ignition criterion Φ_{EC}. The mixture fraction can be expressed by the local equivalence ratio

$$Z(\phi_{loc}) = \frac{y_{O2}^{\infty} - \dfrac{r_{O2} \cdot (1-\phi_{loc})}{\phi_{loc} \cdot (1+r_{O2}) + r_{O2} \cdot (1+ y_{N2}^{\infty} / y_{O2}^{\infty} - \phi_{loc})}}{r_{O2} + y_{O2}^{\infty}} \qquad \text{for} \quad \phi_{loc} \le 1 \quad \text{and} \qquad (4\text{-}5)$$

$$Z(\phi_{loc}) = \frac{\dfrac{r_{O2} \cdot (\phi_{loc} - 1)}{r_{O2} \cdot (1+ y_{N2}^{\infty} / y_{O2}^{\infty}) + \phi_{loc}} + y_{O2}^{\infty}}{r_{O2} + y_{O2}^{\infty}} \qquad \text{for} \quad \phi_{loc} \ge 1 \qquad (4\text{-}6)$$

An analytical solution for $\Phi_{loc}(Z)$ does not exist. To express $\Phi_{loc}(Z)$ a polynomial can be used. This is illustrated using the example of the combustion of hexane. The chemical equation for the reaction of hexane and air to CO_2, H_2O with fixed yields Y_{CO} = 0.008 g/g and Y_{soot} = 0.016 g/g is

$$C_6H_{14} + 9.373\ (O_2 + 0.767/0.233\ N_2) \rightarrow 5.86\ CO_2 + 7\ H_2O + 0.115\ C + 0.025\ CO + 30.853\ N_2 \qquad (4\text{-}7)$$

The stoichiometric air-to-fuel mass ratio for this reaction is

$$r_{O2} = (9.373 * 32\ g/mol)\ /\ 86.06\ g/mol = 3.485 \qquad (4\text{-}8)$$

From Equations (4-5) or (4-6) the stoichiometric mixture fraction becomes Z_{st} = 0.06266.

Concerning the GER-concept, the relevant range where CO yields increase and external combustion starts is between $0.5 < \Phi < 3.0$. For well-mixed exhaust gases, as with the compartment of Gottuk et al., the averaged Φ_{loc} values of the exhaust gases equal the GER. Between $0.5 < \Phi_{loc} < 3.0$ a number of values of $Z(\Phi_{loc})$ is calculated by Equations (4-5) and (4-6). By polynomial regression for the reverse relation $\Phi_{loc}(Z)$ a fourth-order polynomial was obtained

$$\Phi_{loc}(Z) = 24.748 * Z^4 + 13.121 * Z^3 + 15.177 * Z^2 + 15.008 * Z - 0.0033 \qquad (4\text{-}9)$$

For the given range the recalculation by $\Phi_{loc}(Z)$ is in perfect agreement with the analytical $Z(\Phi_{loc})$ values (Fig. 4-12).

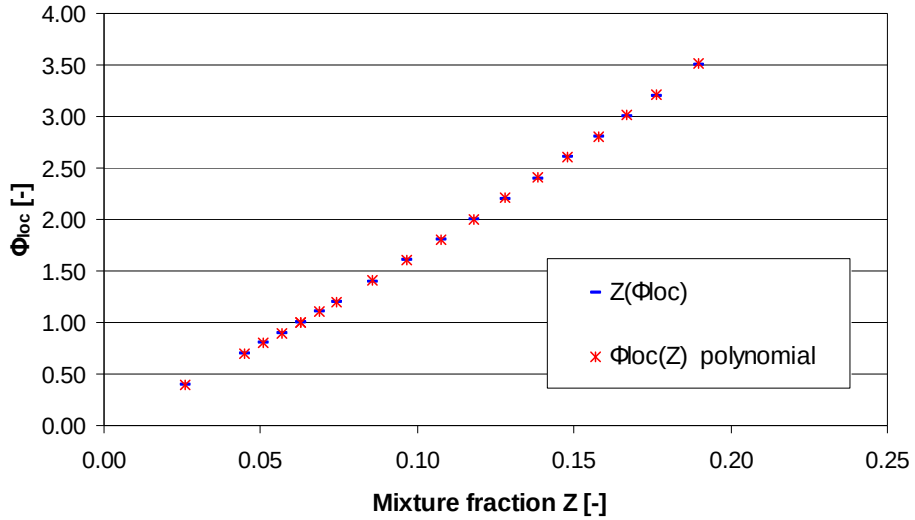

Fig. 4-12. Correlation of Φ_{loc} and Z for a given chemical reaction (Eq. (4-7)). $Z(\Phi_{loc})$ by Equations (4-5) and (4-6) and recalculation $\Phi_{loc}(Z)$ by the polynomial Equation (4-9).

The benefit from the particular construction of Gottuk's prototype compartment with separated inflow and outflow (Fig. 2-9) is also shown in FDS fire simulations (Fig. 4-13a+b). The simulation was performed again with $\delta x = 0.05$ m domain resolution. The prescribed hexane mass loss rate was linearly increased. The hexane reaction is given by Equation (4-7) and the correlation of the averaged local mixture fractions with the local equivalence ratio of the exhaust gases is given by Equation (4-9). For under-ventilated simulations the flame sheet establishes itself above the air distribution plenum and *all* excess fuel is burned at the exhaust vent (Fig. 4-13b). From the experiments sustained external combustion was reported at equivalence ratios exceeding 1.6 (cf. Fig. 3-15). The simulation results are displayed in Fig. 4-14a+b. In Fig. 4-14a it is shown that after the compartment flow dynamics are established, Φ equals $\Phi_{loc}(Z)$ for over-ventilated fires (the deviation between Φ and $\Phi_{loc}(Z)$ represents the compartment's air volume). During the

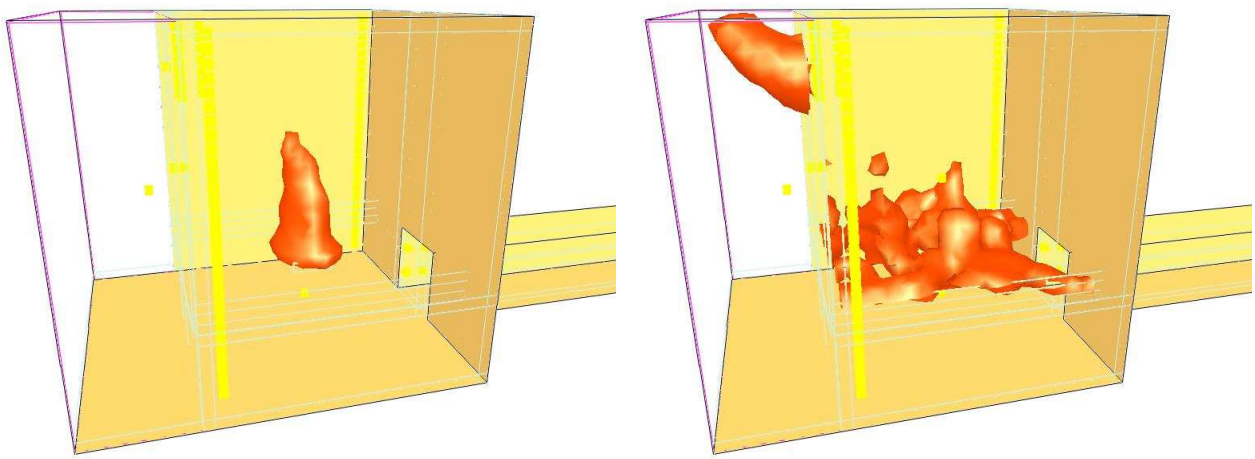

Fig. 4-13a+b. Screenshots of a simulation of Gottuk's compartment (inflow duct from the right). (a) well-ventilated conditions and (b) under-ventilated conditions where the flame sheet is divided into one part covering the air-distribution plenum and a second part indicating external combustion.

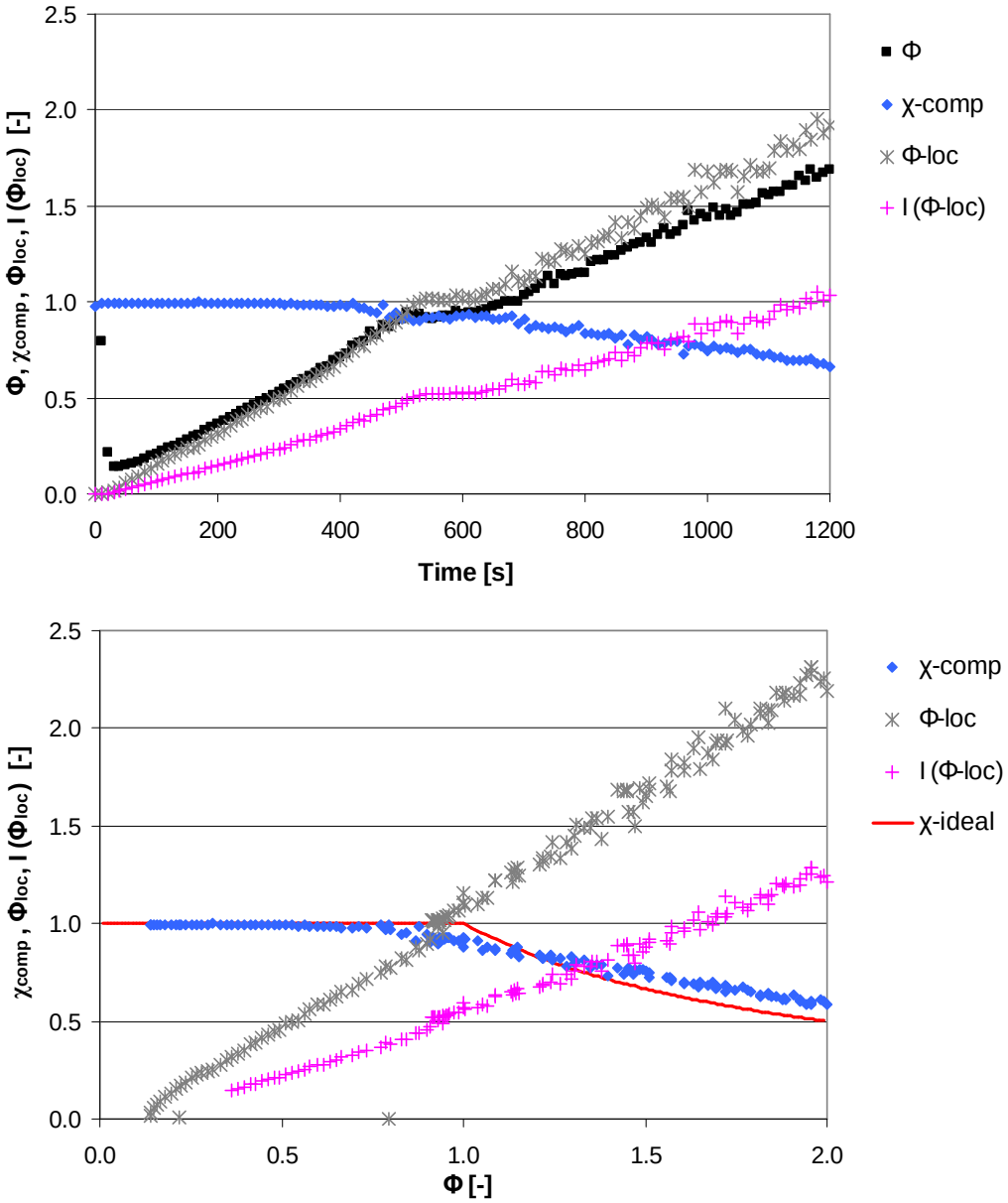

Fig. 4-14a+b. FDS4 simulation results of a hexane fire in Gottuk's compartment (Fig. 2-9) with linearly increased mass loss rate. Behaviour of the GER, the combustion efficiency inside the compartment, the LER and the ignition index over the time (a) and correlation with the simulated GER.

transition to under-ventilated conditions some parameters show a plateau, which results from the relocation of the flame sheet. At $\Phi > 1$ all values are more fluctuating and some discrepancies need to be discussed. Although the polynomial solution of $\Phi_{loc}(Z)$ is very exact, $\Phi_{loc}(Z)$ is predicted higher than Φ from the air inflows. An explanation could be that the compartment inflows were over-predicted. However, when the combustion efficiency χ_{comp} in under-ventilated conditions is compared to the ideal value, it is seen in Fig. 4-14b that more than the ideal heat is released inside the compartment. This would suggest an *under*-prediction of the inflows. The discrepancies are believed to be the result of numerical errors, which obviously increase in under-ventilated conditions. For the purposes of the simulation these errors are in a tolerable range.

The ignition index is calculated by $\Phi_{loc}(Z)$ divided by Beyler's criterion for Φ_{EC} (Eq. (3-39))

$$I(\phi_{loc}, T_{ul}) = \frac{\phi_{loc}(Z)}{-8.135 \cdot 10^{-4} \cdot T_{ul} + 2.36} \tag{4-10}$$

where the T_{ul} is the upper layer temperature close to the exhaust vent. The simulated ignition criterion is fulfilled at $\Phi_{EC} \approx 1.7$. The value is close to the value of $\Phi_{EC} \approx 1.6$ for the beginning of sustained external combustion given by Gottuk (1992) (cf. Fig. 3-15). As this methodology is based on local conditions, it allows for a separate assessment of external combustion at each vent of a multi-vent compartment.

4.4 Conclusions

A state-of-the-art fire simulation tool, the Fire Dynamics Simulator (FDS4), was investigated with respect to its applicability to provide functional simulation results to be used for the GER-concept. As the model so far uses a one-step combustion model, which does not account for changing CO yields, one area of study was the temperatures and resulting mass flows in under-ventilated compartments. While well-ventilated compartment fires were simulated with very reasonable accuracy, for increased equivalence ratios the simulated compartment temperatures were either significantly over-predicted (Fig. 4-3) or the heat release rate inside the compartment broke down and temperatures were seriously under-predicted (Fig. 4-5). An explanation for this behaviour was given.

For the second task of this study, the prediction of flame heights and flame extensions out of an over-ventilated compartment, FDS4 exhibited encouraging results.

The prediction of external burning from under-ventilated conditions lies beyond the capabilities of the combustion model. This constraint was overcome by post-processing Beyler's ignition criterion with FDS output data. With regard to the difficulties which were encountered for the simulations of under-ventilated fires, only Gottuk's prototype compartment (Fig. 2-9) was suited to coherent fire simulation results with Φ exceeding 1 and the precondition that no flame extensions were reported from the experiments. The applicability of the proposed post-processing routine was demonstrated by the simulation of Gottuk's experiments.

The proposed methodology provides a solution in particular cases, but is not applicable when the compartment temperatures are highly under-predicted by FDS4. However, it was announced for the combustion model of the coming FDS5 version that a second scalar besides the mixture fraction is being implemented. With this scalar the actual fuel

concentration will be tracked independently of the mixture fraction. The model will also simulate a two-step reaction with CO as a combustion intermediate (McGrattan 2006b).

5 OTHER TOXIC FIRE GAS COMPONENTS

Carbon monoxide plays the most important role in structural fire deaths from post-flashover fires. With exception of the TOXFIRE experiments, in the experimental studies reviewed above only hydrocarbon and oxygenated hydrocarbon fuels were used. In real fires, construction materials or inventory with various kinds of chemical structures are involved. These contain hetero-atoms like nitrogen, chlorine, and sulphur which generate an unmanageable amount of more or less toxic combustion products. However, it was shown that for most fuels, the acute toxicity of the fire gases is due to a few key species. These are identified in the next section. Then the extent to which the key species can be correlated with the GER is examined. Finally, sample calculations are performed with a toxicity model for an over-ventilated and an under-ventilated situation.

5.1 Toxic key species and toxicity models

Based on an in depth review for the purpose of protection of fire fighters Buff and Greim (1997) considered the species

- carbon monoxide (CO), hydrogen cyanide (HCN), hydrogen chloride (HCl), and formaldehyde (HCHO)

as the most important species to be monitored during accidental fires. Depending on the composition of the fire loads, the list can be extended, with acrolein (CH_2CHO) and sulphur-dioxide (SO_2) being the next relevant species.

An examination of toxic fire gases from plastics performed by Ortner and Hensler (1995) confirmed the significance of the four gases mentioned above. Extension of the list by the less relevant acrolein is also confirmed. Sulphur-dioxide was reported to become important only for fuels with a sulphur content exceeding five mass-percent.

In order to evaluate combinatory effects of the toxic key species, the NIST developed the N-Gas Model (Babrauskas et al. 1998). The model is based on the “well-established” hypothesis that a small number of “N” gases accounts for a large percentage of the total acute toxic potency. A fractional effective (exposure) dose (FED) was defined under assumption of linear additivity of the effects from each species. The model was used with the species carbon monoxide, hydrogen cyanide, hydrogen chloride, hydrogen bromide and it was extended for oxygen depletion and carbon dioxide. The FED is calculated by

$$FED_{NIST} = \frac{m \cdot c_{CO}}{c_{CO2} - b} + \frac{c_{HCN}}{LC_{50,HCN}} + \frac{21 - c_{O2}}{21 - LC_{50,O2}} + \frac{c_{HCl}}{LC_{50,HCl}} + \frac{c_{HBr}}{LC_{50,HBr}} \qquad (5\text{-}1)$$

where the actual atmospheric concentrations c_i of the species i are used. $LC_{50,i}$ is the lethal concentration of the species i referring to 30 min exposure time. The empirically determined parameters m and b were 18 and 122,000 for CO_2 concentrations up to 5 %, and 23 and 38,600 for CO_2 concentrations above 5 %. From oxygen depletion the 30 min $LC_{50,O2}$ is 5.4 %. The other LC_{50} data for the linear terms were $LC_{50,HCN}$ = 150 ppm, $LC_{50,HCl}$ = 3800 ppm and $LC_{50,HBr}$ = 3000 ppm. From the definition of the FED_{NIST}, 50 % of the animals are expected to die at FED_{NIST} = 1 plus or minus a confidence interval. It was reported that due to small non-linearities the 50 % lethality level corresponded to FED_{NIST} = 1.1 with a 95 % confidence interval within ± 0.2.

The most widely accepted dose model currently was developed by Purser (2002). A main difference to the NIST approach is that his FED_{Purser} refers to incapacitation (i.e. disability to escape) of creatures from fire gases. Purser assumed that asphyxiant effects by CO, HCN and irritants are directly additive and that their effects are increased by hyperventilation from elevated CO_2 levels. Additionally the effect of oxygen depletion is considered. Asphyxiant effects of high CO_2 concentrations are considered to be independent from those induced by CO and HCN. Hence, for most practical situations CO_2 causes hyperventilation rather than asphyxiation. As the concentrations vary with time, the partial doses from small time intervals can be added. The total FED_{Purser} can be expressed by

$$FED_{Purser}(t) = \max\left[\sum_0^t \left(\left(F_{CO}(t) + F_{HCN}(t) + FLD_{irr}(t)\right)\cdot V_{Hyp}(t) + F_{O_2}(t)\right), \sum_0^t F_{CO_2}(t)\right] \quad (5\text{-}2)$$

where the fractions of each species are given by

$$F_{CO}(t) = \frac{3.317\cdot 10^{-5}\cdot BMV\cdot c_{CO}^{1.036}(t)\cdot \Delta t}{COHb_{incap}} \quad (5\text{-}3)$$

with the breath per minute volume typically assumed as BMV = 25 l/min for light activity, $c_{CO}(t)$ in ppm, and the concentration of blood carboxy haemoglobin assumed to lead to incapacitation at $COHb_{incap}$ = 30 %

$$F_{HCN}(t) = \frac{\Delta t}{\exp\left(5.396 - 0.023\cdot c_{HCN}(t)\right)} \quad (5\text{-}4)$$

with $c_{HCN}(t)$ in ppm

$$FLD_{irr}(t) = \sum_{i=1}^{n} FLD_{irr,i}(t) = \sum_{i=1}^{n} \frac{c_{irr,i}(t)}{LED_i / \Delta t} \quad (5\text{-}5)$$

Fractional Lethal Dose of irritants contributing to hypoxia (see below)

$$V_{Hyp}(t) = \exp\left(0.2 \cdot c_{CO_2}(t)\right) \tag{5-6}$$

is the factor for hyperventilation from $c_{CO2}(t)$ in vol-%

$$F_{O_2}(t) = \frac{\Delta t}{\exp\left(8.13 - 0.54 \cdot \left(20.9 - c_{O_2}(t)\right)\right)} \tag{5-7}$$

with $c_{O2}(t)$ in vol-%

$$F_{CO_2}(t) = \frac{\Delta t}{\exp\left(6.1623 - 0.5189 \cdot c_{CO_2}(t)\right)} \tag{5-8}$$

with $c_{CO2}(t)$ in vol-%

Incapacitation (practically loss of consciousness) is defined for FED_{Purser} = 1 for the average population. In order to allow for differences in sensitivity and susceptible sub-populations like elderly people or people with coronary heart diseases a FED_{Purser} between 0.1 and 0.3 should be used as an endpoint.

The term FLD_{irr} (Eq. (5-5)) of the fractional lethal dose of irritants is frequently omitted (Purser 2002, Hosser 2006), because the incapacitating effects or irritants are more difficult to determine. If they are to be considered, Purser proposed Lethal Exposure Doses (LED_i) (Tab. 5-1) of main irritants as the denominator in Equation (5-5). The application of Purser's toxicity model with local species concentrations provided by fire simulation with FDS4 (cf. Chapter 4) was demonstrated by the example of a fire in a lecture hall (Forell 2005).

Table 5-1. Lethal exposure doses of irritants contribution to asphyxia and lung damage. Exposure doses predicted to be lethal for half of the population (Purser 2002).

Irritant name	Chemical structure	LED [ppm * min]
Hydrogen chloride	HCl	114,000
Hydrogen bromide	HBr	114,000
Hydrogen fluoride	HF	87,000
Sulphur dioxide	SO_2	12,000
Nitrogen dioxide	NO_2	1,900
Acrolein	CH_2CHO	4,500
Formaldehyde	HCHO	22,500

The most frequently referenced asphyxiant fire effluents are carbon monoxide and hydrogen cyanide. Asphyxiant effects of oxygen depletion and carbon dioxide were additionally considered in the NIST and Purser toxicity models. The most frequently referenced irritant fire effluent is hydrogen chloride whose occurrence is strictly fuel dependent. Other hydrogen halides were noted by the NIST (HBr) and for Purser's model (HBr, HF) and fall in the same category. Of more importance in most cases are organic irritants, namely the aldehydes formaldehyde (HCHO) and acrolein (CH_2CHO). The list of key species ends with the species of SO_2. and NO_2. The fuel dependent generation of SO_2 is obvious whereas for NO_2 the generation from nitrogen in air is less obvious but at least conceivable.

5.2 Applicability of the GER-concept to the key species

The yields of carbon dioxide and oxygen depletion have been shown (cf. Fig. 2-4a+f) to be well described by the approach for products of complete combustion (Eq. (2-3)). With regard to carbon monoxide formation, this approach is slightly conservative. The applicability of the GER-concept to the other key species is best discussed by the generation efficiency of a given fuel hetero-atom in a given fire effluent. The hetero-atoms are nitrogen, halogens and sulphur. In the last section organic fire effluents are discussed.

5.2.1 Nitrogenated fire effluents

Hydrogen cyanide (HCN) is regarded as being about 20 to 40 times more toxic than CO (Purser 2002). It is commonly considered to be produced from N-containing fuels as an intermediate product of the formation of NO_X (Hartzell 1996, Tuovinen et al. 2004). The generation of traces of HCN by nitrogen from air by prompt-NO generation and thermal-NO generation is believed to be of less importance at the temperature levels of accidental fires (Simmons 1995, Blomqvist 2005).

As the generation of NO_X is diminished in under-ventilated conditions (Warnatz et al. 2001, p. 266), it can be assumed that final yields of HCN are increased. This correlation of HCN yields with the GER was suggested by Purser (2003) from experimental findings in a micro-scale combustion apparatus ("Purser tube furnace"). In a later paper under Purser's co-authorship (Fardell et al. 2004) the HCN yields of medium density fireboard (MDF) from experiments in the "Purser tube furnace" and the ISO 9705 room were compared. In the micro-scale the yields increased from close to zero for over-ventilated conditions to a plateau about 0.0035 g/g for under-ventilated conditions ($1.6 < \Phi < 1.9$). With a given

nitrogen content in MDF of 3.69 % the generation efficiency of fuel N to HCN is $Y_{HCN,norm}$ = 0.05 for under-ventilated conditions. For the comparison with the ISO 9705 room it had to be stated (Fardell et al. 2004) that “for HCN the results from the large-scale fires are somewhat disappointing, in that there is no obvious relationship between Φ and HCN yields”. This deviation was attributed to the sampling interval which might have occurred at a fire condition that was not representative for the experiments.

The results of the TOXFIRE ISO 9705 room experiments with N-containing fuels (Ny: 0.124 g_N/g_f, TMTM: 0.129 g_N/g_f) showed a correlation with the amended GER. For nylon the correlation with GER is quite significant and the generation efficiency of HCN from fuel nitrogen exceeds 10 % for under-ventilated conditions (Fig. 5-1). For TMTM the correlation with GER is less significant. The normalised yields are generally lower and in under-ventilated cases the data is more scattered.

As indicated by the above-mentioned large-scale experiments (Fardell et al. 2004), it must be pointed out that the correlation of HCN yields with the GER has proved to be less straightforward in different small-scale experiments (Markert et al. 1999, Bansemer 2004) than that shown in Fig. 5-1. Additional parameters like (flame-) temperatures and residence times seem to be more significant than for CO formation.

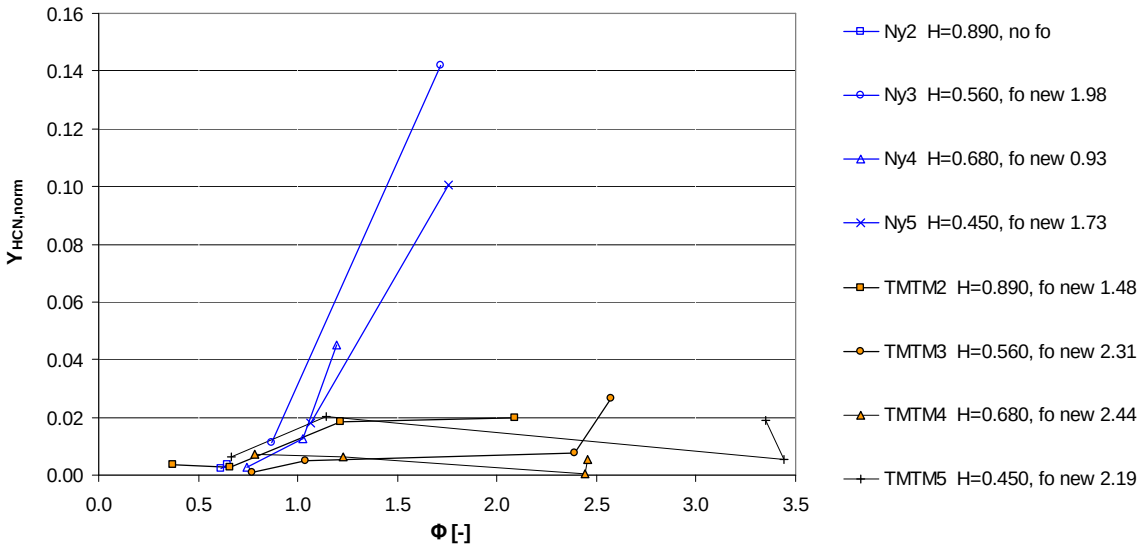

Fig. 5-1. Normalised yields of HCN from fuel nitrogen for Ny and TMTM (calculated from data of Lönnermark et al. (1996)).

Concentrations or yields of nitrogen oxides are frequently reported as lumped NO_X with no exact reference to the NO_2 fraction which is known to be a much more potent pulmonary irritant than NO (Pauluhn 1993). From the TOXFIRE experiments (Sect. 2.4.5) it was reported that NO was the major combustion product with only small amounts of NO_2 measured (Blomqvist and Lönnermark 2001). The general decrease of NO_X yields with increasing GER (Blomqvist and Lönnermark 2001), which is possibly accompanied by an even more significant decrease in the more oxygenated NO_2, is also backed by theoretical

considerations (Warnatz et al. 2001). Formation of ammonia (NH_3), which is of minor toxicological importance, is also known to be enhanced in under-ventilated fires (Lönnermark et al. 1996).

It is assumed that the indicated increase of the HCN yields is more significant than the decrease of NO_2 yields. Therefore, the overall contribution of N-containing species to smoke toxicity is increased in under-ventilated conditions. However, up until now, the data has been less consistent than that for the correlation of CO with the GER.

5.2.2 Halogenated fire effluents

Of the four halogens fluorine, chlorine, bromine, and iodine, chlorine from polyvinyl chloride is of most practical importance. Along with bromine it is also used as a flame retardant. The use of fluorine and especially iodine is less common (Eckel 2004). The formation efficiencies of HF, HCl, and HBr are close to being quantitative (Hartzell 1996). This is also shown by micro-scale experiments on the formation of HCl from chlorine containing fuel (Markert 1996). However, in real fire situations the hydrogen halide concentrations decay quickly in the presence of adsorptive surfaces and water droplets. The TOXFIRE ISO 9705 room experiments (Sect. 2.4.5) with mixed fire loads of 4-Chloro-3-nitro-benzoic acid (CNBA) with PP and of chlorobenzene (CB) showed recovery rates below 60 % (Fig. 5-2). The low values of $Y_{HCl,norm}$ for the CNBA/PP experiments refer to the first averaging interval of each experiment where the walls were cold and much HCl was adsorbed. Surprisingly low HCl levels were also found from full-scale room fires equipped with real furniture (Morikawa et al. 1995). The issue of hydrogen chloride adsorption is treated by Galloway and Hirschler (1994).

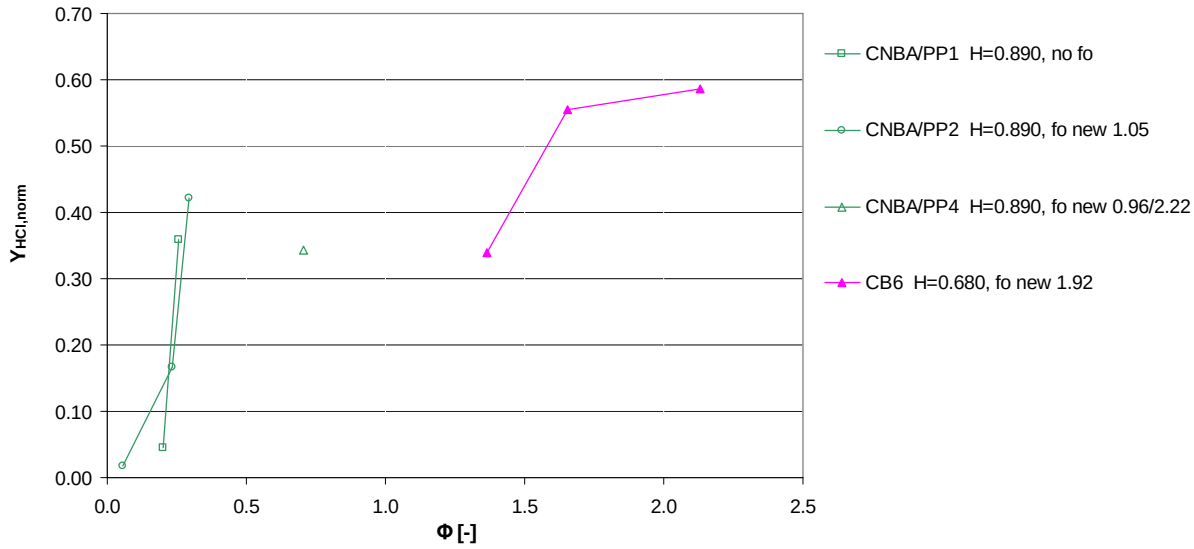

Fig. 5-2. Normalised yields of HCl from fires of CNBA/PP and CB (calculated from data of Lönnermark et al. (1996)).

Regarding the key species of acute toxicity, it can be concluded that the generation of hydrogen halides is not decreased with increased equivalence ratios. With regard to chronically toxic species, halogenated hydrocarbons like dioxins and furans (PCDD/F, PBDD/F) play an important role (cf. Sect 5.2.4). An increased formation of PBDD/F is shown by a recent review of Ebert and Bahadir (2003) for conditions of incomplete combustion.

5.2.3 Sulphur-containing fire effluents

Sulphur dioxide is the most important sulphur-containing fire effluent. From the TOXFIRE large-scale experiments (Sect. 2.4.5) the generation efficiency of SO_2 from TMTM was close to the ideal curve of this product of complete combustion (Fig. 5-3). In under-ventilated conditions a substantial production of carbonyl sulphide (COS) was reported, but yields were not quantified (Blomqvist and Lönnermark 2001). Other notable sulphur-containing species are hydrogen sulphide (H_2S) and carbon disulphide (CS_2) (Buff and Greim 1997). An increased generation efficiency of these un-oxygenated products is expected in under-ventilated condition.

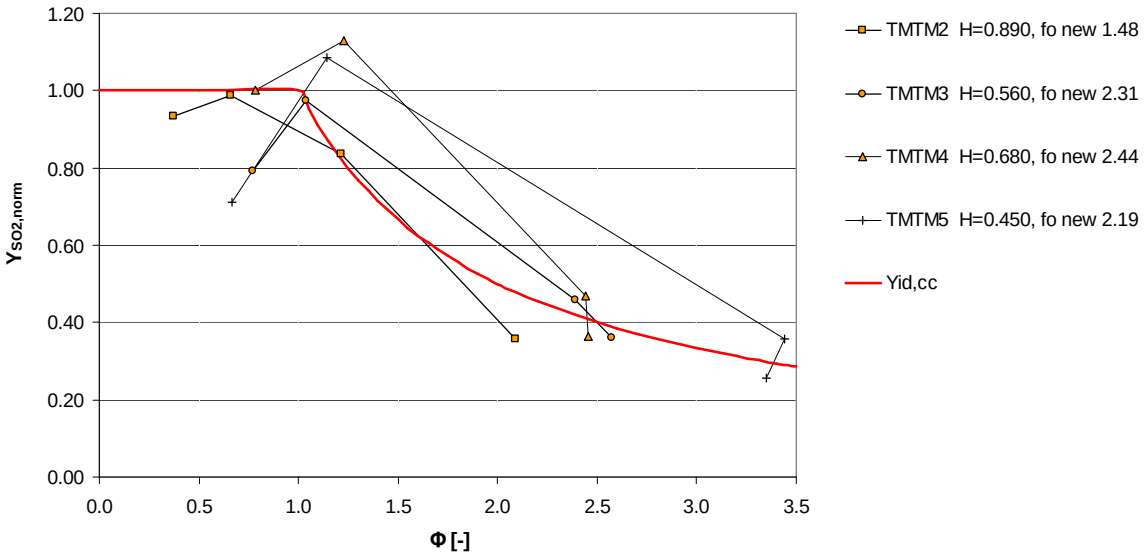

Fig. 5-3. Normalised yields of SO_2 from TMTM (calculated from data of Lönnermark et al. (1996)).

The toxic hazard of the sulphur-containing fire effluents is compared by the ERPG3 values which are published by the US Emergency Response Planning Guideline Committee. The ERPG3 values are defined as the “maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects” (AIHA 2006). As for carbonyl sulphide no ERPG3 is given, the less conservative LC_{50} value of 1 h exposure is taken. In Table 5-2 a normalisation is also given based on the sulphur content of each product

species and a given relative hazard from SO_2 formation of 1. The normalised values clearly indicate that the assumption of full conversion of sulphur to SO_2 is conservative. Under-ventilated fires of sulphur-containing fuels are not believed to increase smoke toxicity of sulphur-containing fire effluents.

Table 5-2. ERPG3 levels (LC_{50} for COS) of main sulphur-containing fire effluents (AIHA 2006) and normalisation by an assumed relative hazard from SO_2 formation of 1.

Name	Chemical structure	ERPG3 [ppm] / LC_{50}, 1h [ppm]	Normalised hazard
Sulphur dioxide	SO_2	15	1
Carbonyl sulphide	COS	1700	0.0088
Hydrogen sulphide	H_2S	100	0.1500
Carbon disulphide	CS_2	500	0.0150

5.2.4 Organic fire effluents

Substantial yields of organic fire effluents are expected from under-ventilated fires (Eq. (2-4)). The organic load is spread over different fractions, which are conveniently divided by their vapour pressure into Volatile Organic Compounds (VOC), Semi Volatile Organic Compounds (SVOC), and Particulate Organic Matter (POM). Due to their high vapour pressure, species of the VOC fraction principally exhibit a better bioavailability for inhalation and pulmonary absorption than species of the SVOC and POM fraction.

The key species formaldehyde (HCHO) and acrolein (CH_2CHO) belong to the VOC fraction. They are predominantly generated under pyrolytic and smouldering conditions (Hartzell 2006), in particular from cellulosic fuels with CHO structures (Buff and Greim 1997). There is no data available from large-scale experiments on the behaviour of these species under different ventilation conditions. Only one small-scale study of formaldehyde generation from wood fires in the “Tewarson-Apparatus” (Tewarson 2002) has been conducted which includes a systematic change of the GER. Although marred by considerable scatter, on average the normalised yields of $Y_{HCHO,norm} \approx 2.5 * 10^{-4}$ for over-ventilated conditions ($0.7 < \Phi < 1.0$) were about 3 times lower than at under-ventilated conditions ($1.7 < \Phi < 3.0$) where a plateau at $Y_{HCHO,norm} \approx 7.5 * 10^{-4}$ was reached (Tewarson et al. 1993). Bearing in mind that the ideal total yield of organic fire effluents (cf. Eq. (2-4)) increases from zero at over-ventilated conditions over $Y_{THC,norm,id} = 0.41$ at $\Phi = 1.7$ to $Y_{THC,norm,id} = 0.67$ at $\Phi = 3.0$, the increase of the fraction of formaldehyde is under-represented.

A similar picture is given by air-controlled experiments in a semi-full scale room with typical furnishings. Morikawa and Yanai (1986) did not report the GER but correlated concentrations of formaldehyde and acrolein with the CO concentrations. Pre-flashover concentrations of both aldehydes were on a relatively constant level. Notably, at this stage their contribution to the overall smoke toxicity could be significant since CO concentrations were rather low. In post-flashover fires concentrations of CO and total hydrocarbon (THC) increased and could be correlated by an idealised linear trend. However, the correlation of elevated CO concentrations with the aldehydes, especially HCHO, was weaker than with THC. That means that formaldehyde in particular loses its significance for smoke toxicity in post-flashover fires.

The NIST (Gann et al. 2003) conducted large-scale fires where the fire conditions were only distinguished in terms of pre-flashover and post-flashover (Table 5-3). The yields of aldehydes from pre-flashover fires of a sofa and a bookcase were significantly decreased under post-flashover conditions. Cable fires under both conditions produced low levels of aldehydes. It is assumed that the high post-flashover temperatures as well as reduced oxygen supply in under-ventilated conditions suppress the generation of significant fractions of aldehydes.

Table 5-3. Aldehyde yields [g/g] from pre-flashover and post-flashover conditions of three fuels with calculated decrease factors (Gann et al. 2003, p. XV).

		Sofa	Bookcase	Cable
Formaldehyde	Yield pre-FO	$< 2 * 10^{-2}$	$< 2 * 10^{-3}$	$< 8 * 10^{-4}$
	Yield post-FO	$< 8 * 10^{-4}$	$< 4 * 10^{-4}$	$< 7 * 10^{-4}$
	Decrease factor	≈ 25	≈ 5	≈ 1.14
Acrolein	Yield pre-FO	$< 8 * 10^{-3}$	$< 2 * 10^{-3}$	$< 4 * 10^{-4}$
	Yield post-FO	$< 1 * 10^{-4}$	$< 1 * 10^{-4}$	$< 1 * 10^{-4}$
	Decrease factor	≈ 80	≈ 20	≈ 4

More stable species of the VOC fraction are methane (CH_4) and aromatic species like benzene. Morikawa and Yanai (1986) also compared the concentrations of methane and THC. Over the full range of THC concentrations which varied from 0 vol-% to 4 vol.-% the fraction of CH_4 accounted for about 0.68 % of the THC. As the data is presented in terms of concentrations and the total composition of the THC remains unknown, the CH_4 mass fraction of THC cannot be quantified but is assumed to have been significant. Methane is not associated with any particular toxic hazard.

A different conclusion is drawn by Blomqvist (2005, p. 38) from experiments on different set-ups including authentic fire scenarios like car fires. Regardless of whether the fuel is aliphatic or aromatic, benzene was the principal organic smoke gas component. For real-scale fire tests with television sets and furniture the benzene content varied between 21 % and 59 % of the VOC. A dependence on the ventilation conditions was not examined. Benzene is known as a potent agent for chronic toxic and carcinogenic effects. Ortner and Hensler (1995) considered benzene as the key species for carcinogenic effects from acute inhalation.

The most frequently examined groups of the SVOC and POM fractions for reasons of chronic toxicology, including carcinogenic effects, are polycyclic aromatic hydrocarbons (PAH) and PCDD/F. Both groups are characterised by chemical stability and long environmental persistence. The behaviour of the main PAH in correlation with the GER from combustion of a herbicide in a micro-scale combustion tube (DIN 1981) was studied by Richter et al. (1999). Since the mass loss rate could not be determined directly, it was determined by the CO_2 generation in the closed system. When ignition occurred in the apparatus the PAH yields were shown to increase significantly over the studied range of about $0.6 < \Phi < 1.7$ and could be well correlated with the GER. As mentioned earlier, the yields of PCDD/F have also been shown to increase under conditions of incomplete combustion (Ebert and Bahadir 2003).

It can be concluded that organic species of incomplete combustion do not become more significant for acute toxicity in under-ventilated conditions. Instead it was shown by comparison in terms of pre-flashover and post-flashover that CO becomes even more significant in acute toxicity. Concerning chronic toxicity, the generation of carcinogenic species like benzene and PAH and PCDD/F of the SVOC and POM fraction has been shown to be enhanced in under-ventilated conditions.

5.3 Application of the FED model for well-ventilated and under-ventilated situations

The influence of changing ventilation conditions on the smoke toxicity is demonstrated by a typical fuel mixture of $C_1O_{0.2}H_{1.5}N_{0.1}$ that is assumed to burn in well-ventilated ($\Phi = 0.3$) and in under-ventilated ($\Phi = 1.3$) conditions. The assumed species yields for both conditions are given in Table 5-4. The FED is calculated according to Purser's (2002) model by Equations (5-2) to (5-8). The increase of the concentration of the combustion products is given by an air dilution factor that starts with 50 times at t = 0 s and is reduced to 1.64 at 600 s

$$DIL(t) = \frac{50}{1.0057^{t}} \tag{5-9}$$

The results for the FED and the fractions thereof are given in Fig. 5-4a+b for both ventilation conditions. In both cases the FED is dominated by F_{CO} together with F_{HCN} which becomes more dominant for increased species concentrations. The F_{O2} from oxygen depletion plays a more important role in well-ventilated conditions than in under-ventilated conditions. The dose of the irritant HCHO is insignificant for the acute smoke toxicity in each case. Although in both scenarios the same amount of fuel is burned, the time-to-incapacitation is reached at t = 596 s and at t = 390 s for the well-ventilated and under-ventilated conditions respectively. In both cases the strong exponential behaviour of Purser's FED shows that the time gap between incapacitation and death, which is assumed at approximately two to three times the incapacitating dose, is short.

Table 5-4. Assumed (normalised) species yields of a sample fuel $C_1O_{0.2}H_{1.5}N_{0.1}$.

	Y_{CO} [g/g]	Y_{HCN}	Y_{CO2}	Y_{O2}	Y_{HCHO}
Well-ventilated (Φ = 0.3)	0.015	0.004	1	1	$2.5 * 10^{-4}$
Under-ventilated (Φ = 1.3)	0.20	0.04	0.77	0.77	$7.5 * 10^{-4}$
Reference	Fig. 2-37	Fig. 5-1	Eq. (2-3)	Eq. (2-3)	Tewarson et al. 1993

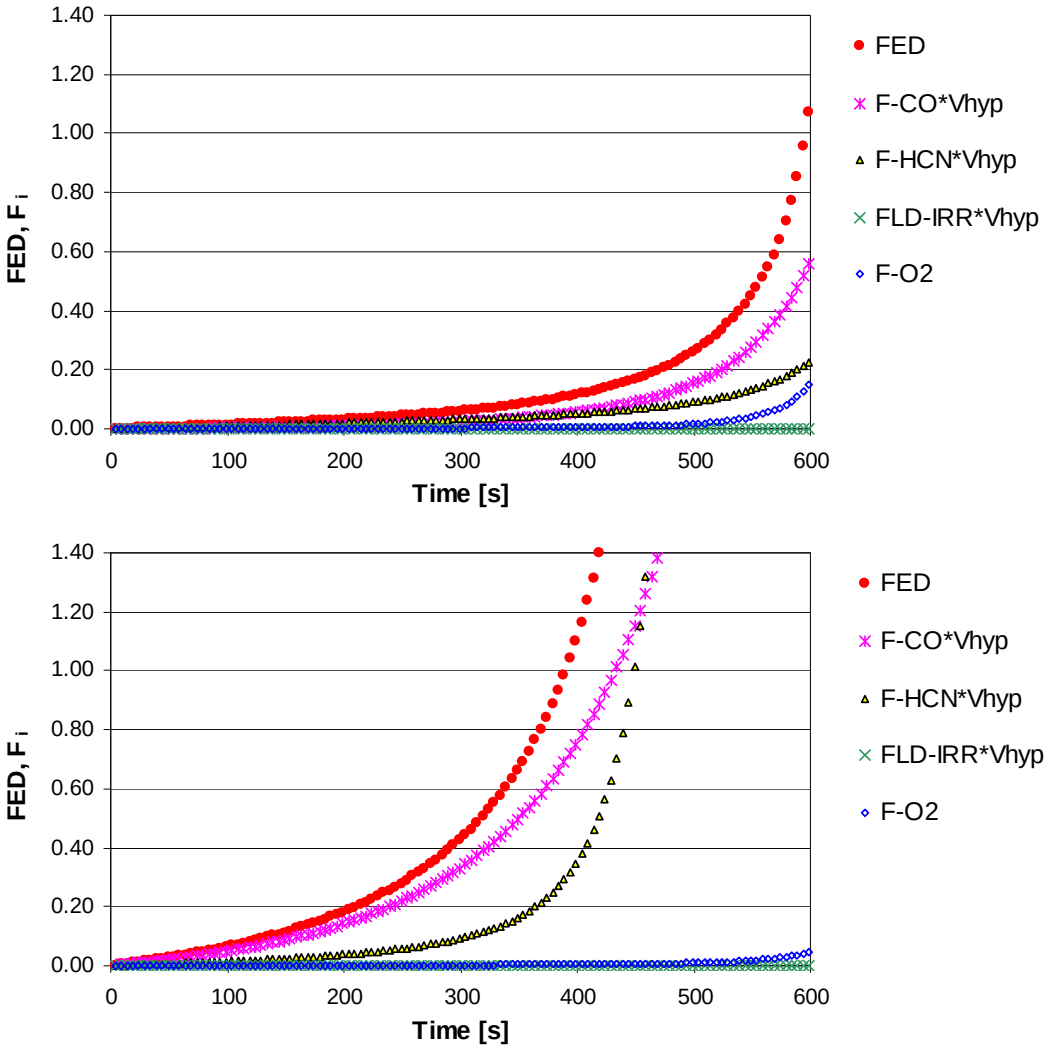

Fig. 5-4a+b. Purser's FED and contributing fractions from a fire scenario in (a) well-ventilated and (b) under-ventilated combustion.

6 CONCLUSIONS AND OPEN QUESTIONS

6.1 Methodology to determine species yields of compartment fires

An extended methodology on carbon monoxide generation in compartment fires by means of the GER-concept can be derived from the findings of this thesis. It includes some refinements compared to that of Gottuk and Lattimer (cf. Sect. 2.4.3). The methodology (Fig. 6-1) consists of two main steps: the determination of the governing equivalence ratio, and the consideration of additional effects such as the upper layer temperature and pyrolysis in the upper layer.

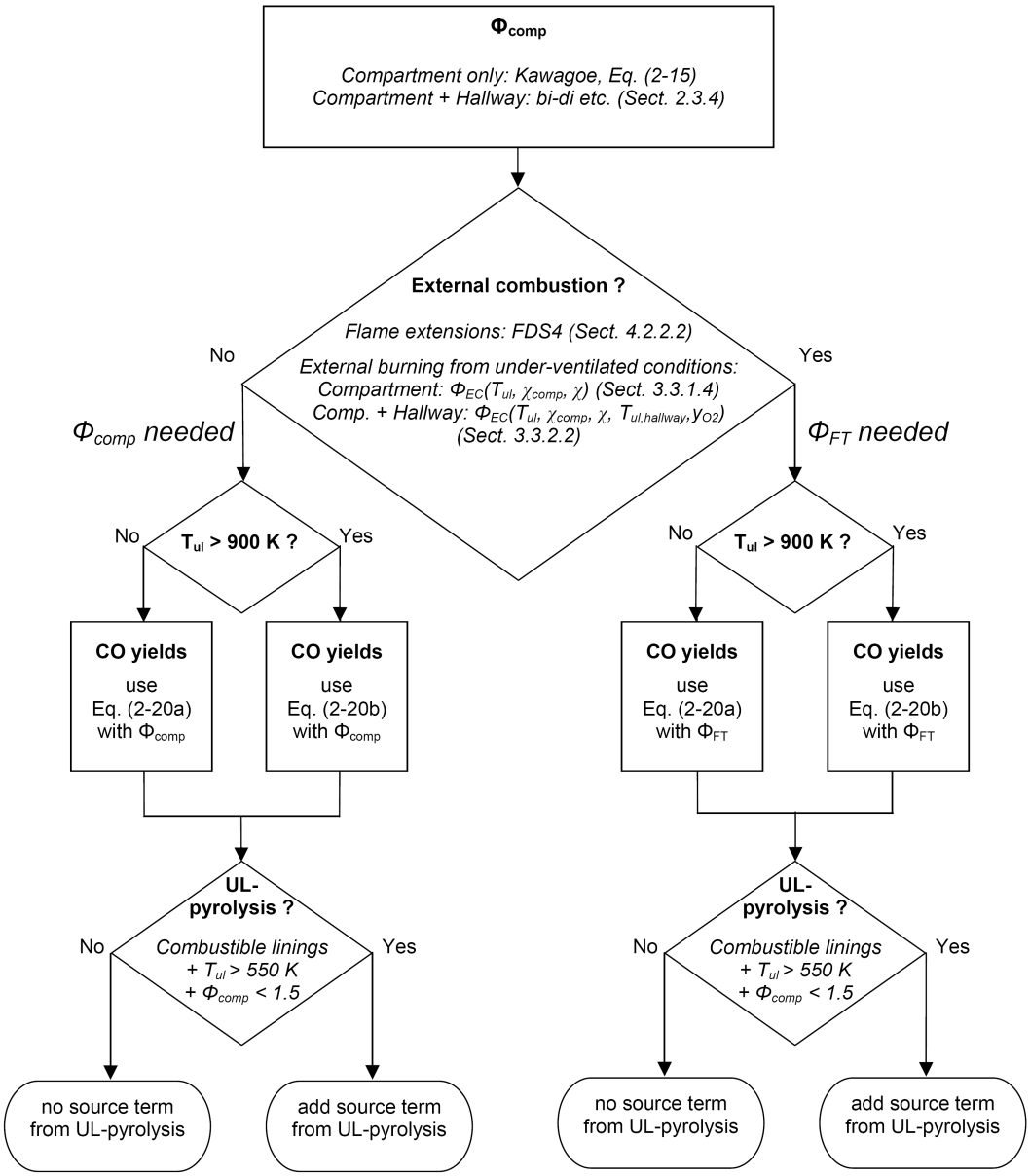

Fig. 6-1. Methodology to determine carbon monoxide generation in compartment fires by means of an extended GER-concept.

The GER of the primary compartment Φ_{comp} is defined by the total mass loss rate including pyrolysis in the upper layer, and by the air inflow. The Kawagoe-Equation (2-15) has been repeatedly shown to provide quite accurate results for the mass flows in a compartment-to-ambient situation. In a compartment-to-hallway situation the flows have to be determined for instance by bi-directional pressure probes (Sect. 2.3.4).

The control volume has to be extended when significant external combustion occurs by flame extensions or due to under-ventilated conditions. In over-ventilated conditions flame extensions have been shown to be assessable with the Fire Dynamics Simulator (FDS4) (Sect. 4.2.2). For assessment of the second phenomenon, extensions of Beyler's equation for $\Phi_{EC}(T_{ul})$ (Eq. (3-39)) are proposed: they account for the combustion efficiency within the compartment χ_{comp} and the overall combustion efficiency χ and have been shown to provide better results for the given validation data (Sect. 3.3.1.4). No data for validation is available for different vitiation conditions in an adjacent hallway. However, the hallway situation was considered in terms of the upper layer temperature $T_{ul,hallway}$, and oxygen concentration y_{O2}. This further extension of the ignition criterion was demonstrated by example (Sect. 3.3.2.2). If a complex examination by $\Phi_{EC}(T_{ul}, \chi_{comp}, \chi)$ or $\Phi_{EC}(T_{ul}, \chi_{comp}, \chi, T_{ul,hallway}, y_{O2})$ is not possible, a rough estimate of external combustion in under-ventilated conditions is given by $\Phi_{EC} = 1.7$ for gaseous fuels with high combustion efficiency and $\Phi_{EC} = 1.9$ for fuels representing typical furnishings. These values do not apply for highly vitiated conditions of the hallway upper layer.

Consistent with the methodology of Gottuk and Lattimer, it is proposed to use either Φ_{comp} or Φ_{FT} as the governing equivalence ratio. Φ_{FT} is calculated by Equation (2-19). The air entrainment and hence the efficiency of external combustion depend on the degree to which the ignition criterion is over-fulfilled.

Since the temperature level $800 < T_{ul} < 900$ K was not defined by Gottuk and Lattimer and since Pitts (Sect. 2.4.4) also assumed considerable upper layer reactions at $T_{ul} > 900$ K, the temperature range to apply the low temperature Equation (2-20a) of Gottuk and Lattimer is extended to $T_{ul} < 900$ K.

Pyrolysis of combustible lining material such as wood in the upper layer at temperatures above 550 K has an additional influence. Re-evaluation of the experiments by Pitts et al. (Sect. 3.2.4) showed that CO yields started to increase even at small equivalence ratios. It is not known yet to what extent upper layer CO from (wood-)pyrolysis is oxidised to CO_2 in a reactive upper layer ($T_{ul} > 900$ K). However, for strongly under-ventilated fires it was shown that CO yields were not further increased compared to Equation (2-20). As CO yields were seen to level off at $\Phi > 1.5$, this value can be taken as a limit where a CO source term from upper layer pyrolysis does not need to be considered separately. The

wood pyrolysis rate must always be added to the mass loss rate for determination of the GER.

6.2 Open questions

There is a gap in the predictive capabilities for external combustion. FDS4 is proposed to assess the occurrence of flame extensions but it was shown that the predictive capabilities of FDS4 start to deteriorate at about $\Phi_{comp} > 0.6$. The degree of ventilation when the deterioration starts depends on the exact geometry of the compartment (Sect. 4.2.2). With Beyler's ignition criterion, flame extensions can only be considered in terms of a reduced combustion efficiency within the compartment (Sect. 3.3.1.4). Hence, there is no means of predicting external combustion for $0.6 < \Phi_{comp} < 1.0$.

Concerning the data which was compiled from experiments in the ISO 9705 room (Sect. 2.4.8.2), some experiments with PP and TMTM from the TOXFIRE project and some experiments with PE from the iBMB project indicated CO yields at $\Phi_{comp} \approx 0.5$, which were higher than predicted by Equation (2-20a). From the discussion of compartment fire dynamics, vitiation of the lower layer by feedback flows is considered as an additional influence (Sect. 3.2.3). Feedback flows are increased for low ratios H/w_v of a given opening vent (cf. Fig. 3-3b). Since the elevated CO yields were not found for smaller vent heights (cf. Fig. 2-37), vitiation effects do not give a consistent explanation. Hence, the data might indicate that Equation (2-20a) does not provide conservative results in some cases.

The influence of combustible lining material in the upper layer was only investigated for wood. Non-oxygenated linings were not investigated. Also the dependence of CO generation by wood pyrolysis on GER is not known for small GERs. It was shown in Section 3.2.4 that CO generation from wood pyrolysis occurs at considerably lower GERs than $\Phi = 1$ as assumed by Pitts (cf. Fig. 2-15). However, the correlation of the additional CO source term with the GER is not known.

Concerning the applicability of the GER-concept to other toxic key species, a correlation of hydrogen cyanide, which was shown to be the most important species, with the GER is assumed but not yet established (Sect. 5.2.1). If the governing effects were known, the methodology could be extended to hydrogen cyanide. CO_2 and SO_2 generation, as well as oxygen depletion, exhibit a clear dependence on the GER. Thus a substantial amount of the overall acute smoke toxicity can be described by means of the GER.

7 SUMMARY

Carbon monoxide (CO) has shown itself to be the most important toxic species in compartment fires. The approach of correlating CO generation in compartment fires with the ventilation conditions has become known as the global equivalence ratio concept (GER-concept). The review of experimental studies on the GER-concept has shown the feasibility of this concept. From re-examination of large-scale experiments in the ISO 9705 room it became clear that the reported mass flows and resulting equivalence ratios have to be amended. The amended data basically confirmed the correlations given by Gottuk and Lattimer. However, for $\Phi \approx 0.5$ and upper layer temperatures below 900 K, elevated CO yields were partly observed which are not covered by Gottuk and Lattimer's low temperature correlation.

The reacting zones in compartment fires are the fire plume and, where the temperature exceeds 900 K, also the upper layer. Examination of the flow dynamics in compartment fires showed that the ventilation conditions of the reacting zones can be expressed by the GER which is a further confirmation of the feasibility of the GER-concept. Feedback flows from the upper to the lower layer and their contribution to lower layer vitiation were examined. This phenomenon has shown to be of limited influence compared with ventilation effects. However, fuel pyrolysis in vitiated upper layers has been shown to lead to increased CO yields. Re-examination of the experiments by Pitts et al. revealed that upper layer pyrolysis also becomes important in well-ventilated conditions ($\Phi < 0.25$).

The GER-concept was extended for external combustion by flame extensions or due to under-ventilated conditions. To assess the occurrence of the second phenomenon, Beyler's equivalence ratio to allow for external combustion Φ_{EC} was extended. In addition to the GER and the upper layer temperature, the combustion efficiency inside the compartment and the overall combustion efficiency were introduced. The extended ignition criterion was in much closer accordance with the given experimental data. Relatively little data is available for the assessment of the efficiency of external combustion, which depends on the ventilation/vitiation conditions of the secondary control volume and the entrainment into the reaction zone. Gottuk and Lattimer made a conservative proposal to consider external combustion only when the external flames reach into the unvitiated upper layer of an adjacent hallway. An alternative approach is presented, in which Beyler's ignition criterion was applied, taking into account the reduced oxygen concentration and elevated temperature in the secondary control volume. These additional factors partly balance each other out.

The numerical fire simulation with the Fire Dynamics Simulator (FDS4) is only partly suited to provide functional simulation results to be used with the GER-concept. Well-ventilated

compartment fires were simulated with very reasonable accuracy which includes the prediction of flame extensions as reported from Wieczorek's half-scale compartment. For increased equivalence ratios the simulated compartment temperatures were either significantly over-predicted, or the heat release rate inside the compartment broke down and temperatures were seriously under-predicted. An explanation of this behaviour was found in an enhancement of the FDS4 combustion model by which an upper boundary is imposed on the local heat release rate of the flame sheet. The combustion model is also not capable of accurately predicting external burning due to under-ventilated conditions. To overcome this constraint, FDS4 output data was post-processed applying Beyler's ignition criterion. The routine was successfully applied for the simulation of Gottuk's experiments.

Besides CO, the acute toxicity of fire gases is due mainly to HCN and CO_2 which also aggravates intoxication by hyperventilation. In addition, oxygen depletion and the asphyxiating effects of irritants such as HCl, SO_2 and aldehydes contribute to acute smoke toxicity. The behaviour of CO_2 and O_2 is well-described by the approach of complete combustion according to the GER. The applicability of the GER-concept to the other key species was investigated by the behaviour of the fuel hetero-atoms and of organic fire effluents under different ventilation conditions. After CO, HCN was also shown to be highly relevant for both ventilation conditions. A correlation of the HCN yields with the GER is assumed but additional parameters are obviously not yet sufficiently defined.

An extended methodology on carbon monoxide generation in compartment fires was derived from the findings of this thesis. The methodology includes some refinements of the methodology of Gottuk and Lattimer. Its main parameter is the governing equivalence ratio which can either be Φ_{comp} or Φ_{FT} for the compartment or for the extended volume reaching to the external flame tip, respectively. The use of the former or latter is decided by the occurrence of external combustion, which is assessed by a complex set of parameters discussed in the thesis. CO yields are predicted by one of two correlations given by Gottuk and Lattimer depending on whether the upper layer temperature is below or above 900 K. A source term from (wood-)pyrolysis may be added if certain preconditions are fulfilled.

ABBREVIATIONS

ABS	Copolymer of Acrylonitrile, Butadiene, and Styrene
AFT	Adiabatic flame temperature
BMV	Breath Minute Volume
CB	Chlorobenzene
CFD	Computational fluid dynamics
CNBA	4-Chloro-3-nitrobenzoic acid
ERPG	Emergency Response Planning Guideline
FDS	Fire Dynamics Simulator
FED	Fractional Effective (exposure) Dose
FLD	Fractional Lethal Dose
FTIR	Fourier Transform InfraRed
GER	Global Equivalence Ratio: equivalence ratio of a defined control volume
HRR	Heat Release Rate
iBMB	Institut für Baustoffe, Massivbau und Brandschutz (Institute of Building Materials, Concrete Construction and Fire Protection)
LER	Local Equivalence Ratio: equivalence ratio at a certain point
LFL	Lower limit of flammability
MLR	Mass Loss Rate
NIST	National Institute of Standards and Technology
Ny	Nylon
PAH	Polycyclic Aromatic Hydrocarbons
PCDD/F	PolyChlorinated DibenzoDioxins/Furans
PE	Polyethylene
PER	Plume Equivalence Ratio: equivalence ratio averaged over the plume area at a certain height, inverse value of the entrainment number
PMMA	Polymethylmethacrylate
PP	Polypropene
POM	Particulate Organic Matter
SVOC	Semi Volatile Organic Compounds

THC	Total hydrocarbon
TMTM	Tetrametylthiuram monosulphide
ULER	Upper Layer Equivalence Ratio
VOC	Volatile Organic Compounds

NOMENCLATURE

Symbols listed with typical dimensions

Latin

A_f	Fuel bed area [m^2]
A_v	Area of a vent [m^2]
B_i	Yield coefficient of species i (Gottuk and Lattimer) [-]
b	Parameter in the N-Gas Model
C	Empirical constant, 0.6 in FDS4
C_V	Orifice coefficient [-]
c	Gas concentrations in toxicity models [ppm] or [vol-%]
c_p	Heat capacity at constant pressure [J/(kg * K)]
D	Effective diameter of the fuel bed/burner [m]
D*	Characteristic fire diameter [-]
f_{ex}	Excess fuel factor [-]
Fr	Froude number [-]
g	Acceleration due to gravity [m/s^2]
H	Height of a vertical vent [m]
ΔH_C	Specific heat of combustion [kJ/kg]
$\Delta H_{C,eff}$	Effective heat of combustion measured in real fires $\Delta H_{C,eff} = \Delta H_C * \chi_{wv}$ [kJ/kg]
$\Delta H_{C,O2}$	Specific heat of combustion per unit mass of oxygen [kJ/kg]
I	Ignition index defined by Beyler [-]
K	Factor in the Kawagoe-Equation, K ≈ 0.52 kg/s*$m^{5/2}$
k	Turbulent kinetic energy of the turbulence
M	Molar mass [g/mol]
m	Parameter in the N-Gas Model
$\dot{m}_f$	Fuel mass flow [kg/s]
$\dot{m}_{fb}$	Feedback flow by shear mixing of exhaust gases with incoming air [kg/s]
m_p	Ratio of the mass of products from burning a unit mass of upper layer gases
N	Entrainment number [-]

n_p	Ratio of the number of moles of post-combustion mixture by moles of pre-combustion mixture [-]
$\dot{Q}$	Heat release rate [kW]
$\dot{Q}^*$	Non-dimensional heat release rate (Zukoski) [-]
$\widetilde{Q}$	Non-dimensional heat release rate (Wieczorek) [-]
r_{air}	Stoichiometric air to fuel mass ratio [-]
r_{O2}	Stoichiometric oxygen to fuel mass ratio ($r_{O2} \approx r_{air} * 0.233$) [-]
T	Temperature [K]
V_{Hyp}	Factor for hyperventilation in Purser's toxicity model
v	Velocity [m/s]
w_v	Width of a vent [m]
δx	Nominal size of a grid cell [m]
X	Mole fraction, volume fraction [mol/mol]
$X_{O2,LL}$	Limiting value of oxygen mole fraction for the FDS4 suppression criterion
Y	Yield [kg/kg]
Y_{norm}	Normalised yield [-]
y	Mass fraction [kg/kg]
Z	Mixture fraction of the fire simulation model [-]
z	Elevation [m]
z_0	Virtual origin of the fire source [m]
z_{fl}	Flame height by definition of 50 % intermittency [m]
z_i	Interface height, boundary between upper and lower layer [m]
z_l	Lowest elevation of gases leaving the compartment (Gottuk and Lattimer) [m]
z_n	Neutral plane height [m]

Greek

γ	Relative smoke layer depth $\gamma = \delta/z_l$ (Gottuk and Lattimer) [-]
δ	Smoke layer depth (Gottuk and Lattimer) [m]
ε	Energy dissipation rate
ζ	Height of external flame over window soffit [m]

ν	Stoichiometric coefficient
ρ	Density [kg/m^3]
Φ	Global equivalence ratio [-]
Φ_i	Equivalence ratio of the control volume i [-]
Φ_{pl}	Plume equivalence ratio averaged over the plume area at the interface height [-]
χ	Combustion efficiency [-]
χ_{wv}	Combustion efficiency for well ventilated fires [-]
χ_{comp}	Combustion efficiency within the compartment [-]

Subscripts

a	Related to ambient conditions
air	Related to air
comp	Compartment
crit	Critical
cv	Convective
dt	Related to the exhaust duct
EC	External combustion
eff	Effective value
f	Fuel
fl	Flame
FT	Flame tip (Gottuk and Lattimer)
id	Ideal conditions
in	Related to inflow
inert	Related to inert species
l	Low
ll	Related to the lower layer
loc	Related to local property
out	Related to outflow
O2	Oxygen

op	Related to the opening
p	Related to products
pl	Plume
ref	Reference value
rel	Relative value
st	Stoichiometric
SL	Stoichiometric limit
temp	Value calculated from temperature measurements
ul	Related to the upper layer
v	Vent
w	Wall
wv	Related to well-ventilated conditions
∞	Final value

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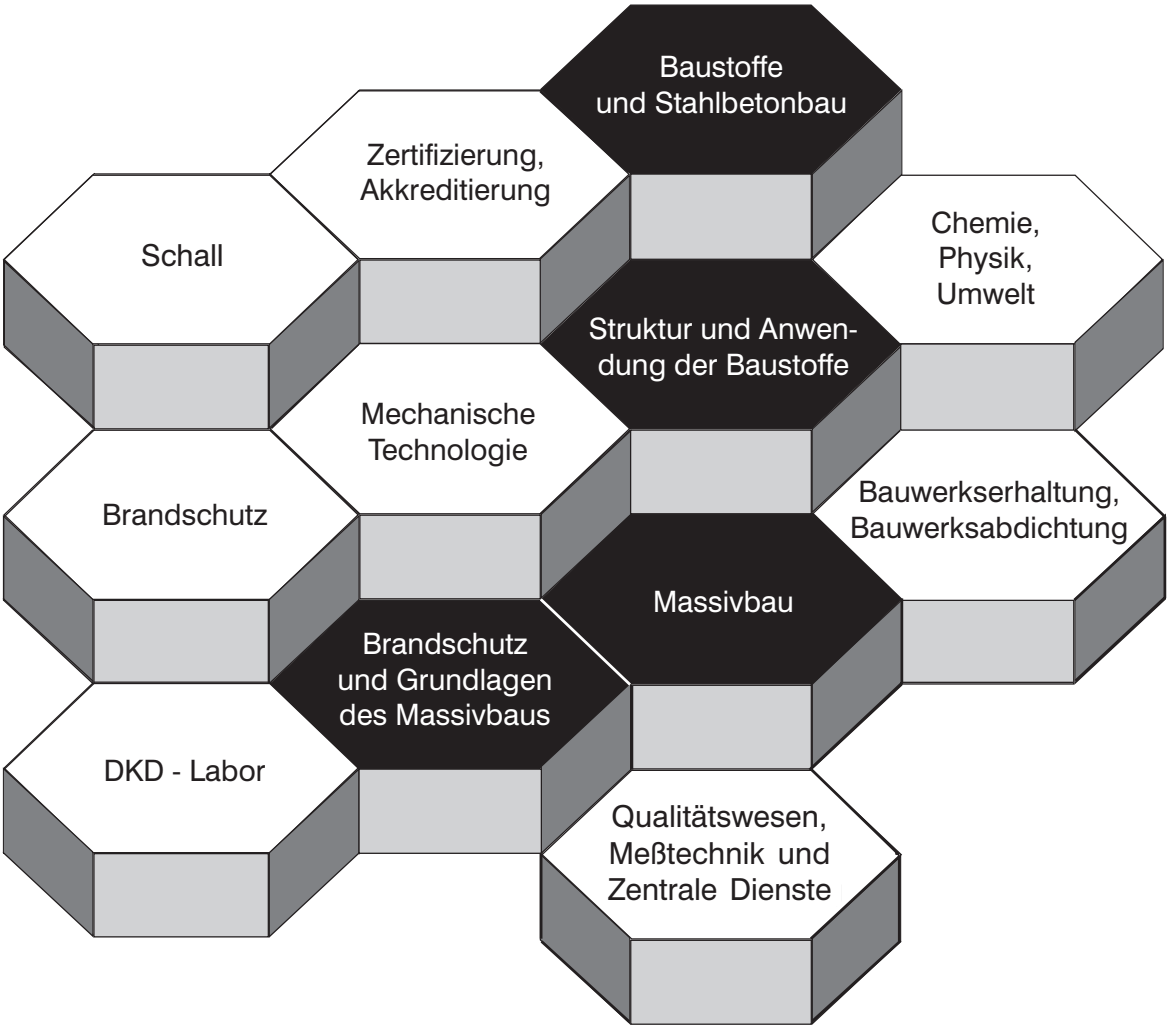

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