Carbon Monoxide and Smoke Production Downstream of a Compartment for Underventilated Fires

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ABSTRACT
The carbon monoxide, carbon dioxide and smoke yields measured downstream of a small scale compartment (volume 0.125m$^3$ – 0.375m$^3$) were studied for underventilated fires of propane. The flow rate of propane was increased gradually and species were collected under a hood. The heat release rate (HRR) of the combustion products was also measured (by oxygen depletion) and was found to initially increase as the flow rate of propane was increased (overventilated burning inside the compartment). Before external burning started, an intermediate plateau in the measured HRR was observed, corresponding to the Heat Release Rate $=1500AH^{1/2}$, where A and H are area and height of the opening respectively. The same behaviour was observed for all openings and remarkably all compartment geometries employed in this work. Further experiments indicated that the occurrence and extent of that plateau depends on the temperature inside the compartment and thus the growth rate of fire. Species production during this plateau period was investigated, as combustion was underventilated during this phase. It was observed that carbon monoxide (CO) and smoke yields increased during this period. The CO yield increased by a factor of 5, whereas the smoke yield by a factor of 3. Moreover, comparison and differences are discussed between the values of the ratio of carbon monoxide to smoke yield from our study and from the literature. The present results for the increased amounts of carbon monoxide and smoke are applicable if, during the fire growth, underventilated conditions develop without external burning. Current engineering calculations for smoke and carbon monoxide can not predict the high concentrations of carbon monoxide and smoke measured in such a scenario. Whether these conditions can be developed will depend on whether the gas temperatures at the opening of the enclosure are able to ignite the unburned gases issuing from the enclosure. This in turn, depends on the fire growth rate, i.e. for a fast increase in the fuel supply rate the gas temperatures in the enclosure are lower than for a slower increase in the fuel supply rate due to (transient) heat losses to the walls of the enclosure and as result outside burning starts much later.

KEYWORDS: compartment fires, smoke, toxicity, carbon monoxide; smoke yield; underventilated combustion.

NOMENCLATURE LISTING

<table>
<thead>
<tr>
<th>Characteristic/Expression</th>
<th>Symbol</th>
<th>Unit</th>
</tr>
</thead>
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<tr>
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<td>$A$</td>
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<td>Height of the opening</td>
<td>$H$</td>
<td>m</td>
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<td>Ratio of the intensity</td>
<td>$I_s/I$</td>
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<tr>
<td>Light extinction coefficient</td>
<td>$k$</td>
<td>m$^3$</td>
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<td>$L$</td>
<td>m</td>
</tr>
<tr>
<td>Mass produced</td>
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<td>kg/s</td>
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<td>Mass loss rate</td>
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<td>kg/s</td>
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<tr>
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<td>m$^3$/s</td>
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<tr>
<td>Yield</td>
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<td>g/g</td>
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</table>

Greek

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<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$\phi$</td>
<td>Global Equivalence Ratio (GER)</td>
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<tr>
<td>$\sigma_f$</td>
<td>Specific Extinction Area on fuel mass loss basis</td>
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<tr>
<td>$\sigma_s$</td>
<td>mass-specific extinction coefficient</td>
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Subscripts

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<tr>
<td>$Co$</td>
<td>carbon monoxide</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>carbon dioxide</td>
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<tr>
<td>$f$</td>
<td>fuel</td>
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<td>$s$</td>
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INTRODUCTION

In recent years the number of fire fatalities in the UK has tended to decrease, however still about 50% of them are due to smoke inhalation. In addition to that, about 18% of deaths are related to smoke and burns together, so the conclusion is that about 70% of fire fatalities in the UK are related to some extent to smoke and toxic gases. Regarding non-fatal casualties, 33% of them in the year 2005 were due to the effects of gas and smoke [1]

One of the reasons for such a high number of fatalities is due to the toxicity of smoke particulates and gases from the fire. Carbon monoxide, a smoke component which is a product of incomplete combustion, augments the overall toxicity of these products to a great extent [2], [3].

Since haemoglobin in the blood has a stronger affinity to carbon monoxide (CO) than to oxygen, the amount of oxygen (in the form of oxyhemoglobin) transported to all tissues decreases when people are caught in a dwelling fire. The time to incapacitation due to carbon monoxide inhalation can be as little as a few minutes, and for fully developed fires even less than 1 minute in close vicinity of the fire origin [2].

In addition, a victim usually doesn’t know that there is a high concentration of carbon monoxide in the atmosphere, because the only signals given by the body are headaches or nausea. Even more, at this stage it may be too late, because these symptoms can be rapidly followed by unconsciousness. Purser [2] highlights also that the onset of severe effects is sudden and thus very dangerous. In addition, the response of every person to high concentrations of carbon monoxide depends on the volume of air breathed, because the amount of carbonhemoglobin depends linearly on it. Consequently, people who wake up during a fire and only start to evacuate after waking up are prone to be more seriously affected. Moreover, small children are more prone to this effect, because the ratio of volume of air breathed to kilogram of body mass is greater for them. Therefore the time for incapacitation for children is shorter than for adults [2]. If one adds the fact that children are “deep sleepers” and research [4] has shown that normal smoke alarm noise may not wake them up, it is obvious than the danger related to carbon monoxide is of crucial importance for children.

Finally, even after successful recovery of the victim, carbon monoxide is responsible for delayed neuropsychiatric sequels, described in many references, for instance in [5], [6]. These symptoms can occur within a few days, or several weeks after an incident, and are related to changes in the brain structure. As a result many severe disorders can develop, such as “lethargia, behaviour changes, forgetfulness, memory loss and Parkinsonian features” [7].

The problem of carbon monoxide production in enclosure fires has been studied for many years; important outcomes are described for instance by Gottuk and Lattimer [8]. They also proposed a detailed engineering approach to predict the yield of carbon monoxide as a function of a Global Equivalence Ratio (GER) and temperature. However, this method characterises carbon monoxide inside a compartment, and not outside. Nevertheless, Gottuk with co-workers also conducted a study [9], to characterise the yield of CO in locations downstream of the compartment and the effect of external burning [9], however no correlations were proposed, especially in cases when escaping gases do not ignite.

Our research is aimed at the further investigation of carbon monoxide and smoke production before external burning. Among others, one possible application of this paper is the case of a fire in a high-rise building, when smoke emerging from a window at one floor affects the higher stories. This issue is becoming more important nowadays, as more skyscrapers are being built all over the world. A similar scenario can be possible on big cruise liner ships and sea ferries, which are multi-storey constructions and are often occupied by thousands of people.

The structure of the paper is as follows. First, the experimental conditions and methodology are described, followed by the section devoted to our results. Finally conclusions are presented.

EXPERIMENTAL CONDITIONS

The experiments were conducted in three different geometries, which were constructed from cubic modules, 0.5m x 0.5m x 0.5m each. The first geometry was made from one module (box A), whereas the second and the third were made from two (A+B) and three (A+B+C) respectively, as illustrated in Fig. 1. The amount of air available was varied by using different openings sizes in the front panel. All openings were door like having widths and heights respectively: 7.5cm x 20 cm, 10cm x 25cm, 20cm x 20cm. Only
one fuel, propane was used. Gas was supplied from a rectangular (10 x 20cm) sandbox burner controlled by a mass flow controller. The sandbox burner was located in the middle of box A in the geometry of one box, in the middle of box A or box B in the geometry of two boxes and in the middle of box A, box B or box C in the geometry of three boxes.

![Diagram of experimental compartment]

**Fig. 1.** Top view of the experimental compartment.

During the experiments the following measurements were made:

a) gas temperatures inside the compartment by thermocouple trees at two corners as indicated in Fig. 1. Type K Sheath thermocouples with bead size 1.5 mm were used for measuring gas temperatures.

b) actual heat release rate, obtained by placing the compartment under a calorimeter hood and analysing the combustion gases [10].

c) smoke concentration obtained from light extinction measurements in the exhaust duct (0.4m diameter) with a 632.8 nm He-Ne laser, 3mW. The signal from the laser beam was passed through a beam splitter in order to monitor intensity fluctuations [11], [12].

d) carbon monoxide and carbon dioxide concentrations, obtained after exhaust gas samples were passed through H₂O traps, containing Drierite (active ingredient CaSO₄).

A detailed description of these experimental conditions and measurements is presented in [13], [14].

**METHODOLOGY**

This section describes the methodology applied during our tests. Firstly, the experimental fire growth is described, which is followed by the discussion on the observed Heat Release Rate and how the Global Equivalence Ratio was derived before external burning. Then data reduction for the carbon monoxide, carbon dioxide and smoke yields is discussed followed by description of how our data were smoothed.

**Fire growth**

In order to establish quasi-steady state conditions inside the compartment, the flow rate of propane was increased gradually, until the desired flow (or theoretical heat release rate) was reached. The flow rate was increased by small steps, however the flow was approximated by a linear fit for the calculations. While the fuel supply rate was being increased, the actual heat release rate was monitored by the calorimeter. Every experiment was aiming for underventilated conditions, according to the procedure described below.

A typical history of Heat Release Rate (HRR) is presented in Fig. 2. The theoretical HRR is represented by two curves: the solid one for the HRR calculated from the fuel supply rate (gradual increments) and the dashed curve which represents linear a fit used in the calculations. The line labelled Q_{vmax} represents the maximum HRR, which is possible for ventilation controlled burning inside the enclosure and it is discussed below.

It can be seen in Fig. 2 that the theoretical and actual values of HRR are the same before an intermediate plateau is reached in the measured HRR (from about 300 to 580 seconds in Fig. 2). Inspection and comparison shows that the intermediate plateau value of the HRR is equal to Q_{vmax}=1500AH^{1/2} (kW), where A (m²) and H (m) are the area and height of the opening, respectively [14], [15]. The value of Q_{vmax} is
derived by multiplying the ventilation controlled mass flow of air [13] into the compartment (Eq. 1) by the energy released per kilogram of air completely consumed inside (about 3000 kJ/kg) [13]:

\[ m_a = 0.5AH^{\frac{1}{2}} \text{ (kg/s)} \]  

(1)

![Graph showing HRR history for test with 2 boxes geometry and opening size 0.1m*0.25m. Fuel: propane.](image)

Fig. 2. HRR history for the test having 2 boxes geometry and opening size 0.1m*0.25m. Fuel: propane.

During this period, flames existed only inside the compartment with excess pyrolysate escaping outside the compartment without burning. When flames outside the compartment were first observed the HRR measured by the calorimeter suddenly increased to the value corresponding to the designed steady state heat release rate. The same behaviour was observed for all openings and remarkably all compartment geometries employed in this work. This behaviour was explained in [14] and [15], and is further discussed in the section on our results.

Furthermore, during this phase, the theoretical heat release, computed from the propane supply rate, was larger than measured by the oxygen depletion, so underventilated conditions occurred until flames emerged from the opening. This time period is marked by grey shading on Fig. 2. Moreover, the presence of this plateau allowed us to derive the mass flow rate of air into the compartment from Eq. 1 not only for quasi steady state conditions [16], [17], but also for this intermediate period. This allows us to derive a Global Equivalence Ratio [18] as explained in the next subsection.

**Global Equivalence Ratio**

In order to calculate the Global Equivalence Ratio (GER) [18] for a given control volume, the mass entrainment of air must be determined. In the case of an enclosure fire, Eq. 1 can be applied only for post-flashover conditions, i.e. quasi steady state [16], [17]. The temperature distribution and the height of the neutral plane needs to be known for transient conditions [16], [17].

However, as it was explained in the previous section, Eq.1 can be successfully applied for the underventilated intermediate plateau period (Fig. 2), i.e. when the HRR is almost constant before external burning occurs. For this period, the theoretical heat release, computed from the propane inflow rate, was bigger than measured by the oxygen depletion, so for this period underventilated conditions occurred.
However, after the flames emerged from the opening, they reacted with the outside air available, and thus the combustion was no longer underventilated. Therefore, the global equivalence ratio concept could be applied for the period when the heat release rate reached an intermediate plateau (Fig. 2) and until the flames started appearing outside of the enclosure. This time period is marked by grey colour on Fig. 2.

For this period, the GER was calculated from Eq.2, where $HRR_{theoretical}$ is the theoretical Heat Release Rate derived from the known supply rate of propane and the denominator is the maximum HRR for the given opening size ($Q_{vmax}$ in Fig. 2) [13], [14]:

$$\phi = \frac{HRR_{theoretical}}{1500AH^{1/2}}$$

(2)

**Carbon monoxide and carbon dioxide**

The yields of CO and CO$_2$ were calculated as the amounts of CO and CO$_2$, respectively, generated in the course of fire divided by the mass loss rate of fuel.

$$Y_{CO} = \frac{m_{CO}}{m_f}$$

(3)

Most gas analysers require that the mixture of gases is dried before it reaches the apparatus, therefore the reported volume fractions are on dry basis. However in reality the concentrations will be lower, because of water present in the combustion gases. The actual difference between wet and dry fractions depends on the H$_2$O concentration and usually is 10 to 20 percent by volume [8]. Therefore our measurements were corrected according the procedure in [19].

**Smoke**

Light extinction measurements were made to obtain the light extinction coefficient $k$ ($m^{-1}$):

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

(4)

where: $L$ – path length through smoke, in our duct $L=0.4m$; $I_0/I$ - ratio of the intensity of incident light to the intensity of transmitted light (\).

A 3 mW He-Ne laser of a 632.8 nm wavelength was used and from these measurements the smoke yield (g/g) was calculated, defined as the mass of smoke produced by the mass loss of fuel. The smoke yield can be obtained either by weighting the mass of soot particulates collected on a filter [20], or also derived from light extinction measurements, provided that the mass loss rate of fuel is known. The latter approach is described for instance by Tewarson [21], and a similar methodology is proposed by Mulholland [12]. In our experiments the methodology proposed by Mulholland was adopted and the smoke yield was calculated as:

$$Y_s = \sigma_f / \sigma_s$$

(5)

The numerator is sometimes called Specific Extinction Area on fuel mass loss basis ($SEA_f$), and is commonly used for instance to report results related to smokiness of a sample in the Cone Calorimeter Test [11], [22], [23]. It can be calculated as follow [11]:

$$\sigma_f = k \dot{V} / \dot{m}_f$$

(6)
where: \( \dot{V} \) - volumetric flow rate through the duct, corrected to ambient conditions [24]; \( m_f \) - mass loss rate of fuel (g/s).

The denominator of Eq. 5 is \( \sigma_e \), sometimes called mass-specific extinction coefficient. The underlying assumption [12], [21] is that this value is constant. This hypothesis allows one to calculate the smoke yield only from light extinction measurements. However there is significant difference in the value proposed by Mulholland and Tewarson. For this study a value of \( \sigma_e \) equals 8.7 (m²/g) was used, taken from [12]. It is believed that the value proposed by Mulholland is more accurate, as he conducted a review of many experimental data [25] and suggested a value 8.7 ± 1.1 (m²/g) for most hydrocarbons in over-ventilated combustion. In contrast, Tewarson is using \( \sigma_e \) about 10.0 m²/g, which comes from only one source, the earlier research by Newman and Steciak [26]. In the original paper [26], a dimensionless mass extinction coefficient 7.0 was given, together with the density of soot particulate 1.1 g/m³. Based on that, one can readily establish \( \sigma_e \) as about 10.0 m²/g.

Data smoothing

Finally, all data on the graphs were centrally averaged and presented as 60 sec average [24].

RESULTS AND DISCUSSION

This section presents the results from our experiments followed by a discussion. In the first subsection, the smoke, \( CO \) and \( CO_2 \) yields measured outside of the compartment and before external burning, are characterised. The second subsection discusses the ratio \( \dot{Y}_{CO}/\dot{Y}_s \), as a parameter recently analysed by Tewarson, [27]. We compare his results with our data and data published by Gottuk [28] and try to account for encountered differences. Finally, a discussion on the temperature distribution inside the compartment is presented.

Species yields

Figure 3 presents typical curves of smoke, \( CO \) and \( CO_2 \) yields together with the HRR during one experiment for an 1 box geometry. The grey shading part indicates the region of underventilated conditions before external burning starts. All values are smoothed by 60 sec central averaging.

It can be seen that the \( CO \) and smoke yields increase during underventilated conditions before external burning. The \( CO \) yield could increase about by factor of 5, whereas the smoke yield by a factor of 3. Moreover, the maximum value of the carbon monoxide yield can be observed just before flames appear outside, this is the same for the smoke yield.

The reason for this behaviour is related to the external combustion [28]. Moreover, it may be assumed, that before external burning starts, the smoke, \( CO \) and \( CO_2 \) yields as measured downstream of the compartment are the same as inside the compartment, because there may be no reduction without external burning. This hypothesis will be examined in future tests.

Repeatability/Uncertainty

Some of the experiments were repeated showing good agreement with previous tests however lack of time didn’t allow us to run tests to quantify the \( CO \) and smoke (\( Y_s \)) yields confidence levels. This work is currently ongoing. Notwithstanding, the major uncertainty in the yields lies in the variation in the duration of the plateau, which may last for a few seconds to up to several hundreds seconds before flames appear outside the compartment. The duration of the plateau (underventilated conditions) appears to be largest for fast burning rates and/or larger compartments, (when the compartment walls are still relatively cold and heat losses to the wall are large) resulting in larger \( CO \) and smoke yields during the underventilated burning inside the compartment. Nevertheless, the variability in the \( CO \) and smoke yields as a function of the GER is no more than ±20% for the wide range of conditions tested (see Fig. 4), yet over one order of magnitude larger than the steady-state values (overventilated conditions).
Consequences

This may lead to the conclusion that in the case of fire in a high-rise building or a passenger ship, before external burning, a lot of smoke and CO may be transported outside, which may strongly affect conditions far away from fire origin. However, as external burning starts, smoke and CO decline significantly. This issue may be important for organising an evacuation during the first period of fire, as high concentrations of smoke may be encountered on stories or decks above the place of fire origin.

Fig. 3. Heat Release Rate together with the smoke, CO and CO2 yield. Fuel: propane. Opening size 0.1m*0.25m. 1 box geometry.

Relationship between the CO yield and the smoke yield.

It was recently suggested by Tewarson [27] that there is a constant ratio between the carbon monoxide yield and the smoke yield, at least for overventilated conditions. He suggested that the ratio $Y_{co}/Y_s$, is about $0.34 \pm 0.05 \text{ (g/g)}$ for hydrocarbons during overventilated conditions, “where soot is formed via the polycyclic aromatic hydrocarbons (PAH) precursors” [27]. However our tests for propane during underventilated burning showed significantly higher values of about an order of magnitude (Fig. 4). Moreover, this ratio wasn’t constant and increased for higher equivalence ratios.

In Fig. 4, this ratio is plotted together with the smoke and carbon monoxide yields as a function of the Global Equivalence Ratio (GER) [18]. The chosen range corresponds to the grey shaded part of Fig. 2 and Fig. 3, i.e. underventilated conditions before flames emerge out of the opening. Our data was adjusted so there was no time shift between CO and smoke yields.

It can be seen that the yields of both products of incomplete combustion, i.e. carbon monoxide and smoke tend to increase for higher equivalence ratio, however this increase is much faster for the carbon monoxide yield. As a result, the ratio $Y_{co}/Y_s$ is increasing too, almost linearly.

In order to validate our results, the data published by Gottuk were also examined [28].

Comparison with Gottuk’s study

Gottuk conducted a study of a compartment with separated inflow of air. That design allowed him to derive accurate information about mass of air entrained and thus the plume equivalence ratio [8], [28]. Among others, he presented data for hexane fire with external burning, where the sampling point was downstream
of the compartment (Fig. 5.4 in [28]). In order to compare similar conditions, only data for the plume equivalence ratio greater than one was examined, corresponding to underventilated conditions. Moreover, our control volume for GER calculations was limited to our compartment, therefore Gottuk’s plume equivalence ratio can be compared with our GER values. In addition, only the data points before external burning were examined. In order to have similar procedure for smoke yield calculations, his data were recalculated with constant value 8.7 m$^2$/g instead of 10 m$^2$/g, as explained previously.
Fig. 4. The smoke and CO yields together with the ratio \( Y_{\text{co}}/Y_s \) as a function of the GER. Fuel: propane.
(a) Opening size 0.1m*0.25m. 1 box geometry. (b) Opening size 0.2m*0.2m. 2 boxes geometry.
(c) Opening size 0.2m*0.2m. 3 boxes geometry.

The ratio \( Y_{\text{co}}/Y_s \) derived from his data was in the range of 6.3 to 15.2 (g/g), whereas in our experiments the ratio was in the range of 2.1-13.2. These figures don’t differ significantly and they are one order larger than for overventilated combustion\[27\]. This confirms that the ratio \( Y_{\text{co}}/Y_s \) is much higher for underventilated combustion.

The observation that the ratio \( Y_{\text{co}}/Y_s \) is not constant for underventilated conditions was made earlier by Leonard and co-workers \[29\]. They suggested that for underventilated conditions, the carbon monoxide yield was not sensitive to fuel type, whereas the smoke yield was affected by fuel type. However, they conducted that study in a Burke-Schumann type burner and this problem needs a further investigation to include for instance a possible effect of residence time and temperature.

The present results for the increased amounts of carbon monoxide and smoke are applicable if, during the fire growth, underventilated conditions develop without external burning. Whether these conditions are being developed will depend on whether the gas temperatures at the opening of the enclosure are able to ignite the unburned gases issuing from the enclosure. This problem is dealt with in the section to follow.

Temperature

Recent tests \[30\] have shown that the presence of the intermediate plateau of the HRR (Fig. 2 and Fig. 3) may depend on the temperature of the upper layer, i.e. for temperatures higher than 1000 °C there was not such a plateau. The temperature history was associated mainly with the fire growth rate, i.e. for the slower increase in the fuel supply rate (2000 seconds) higher temperatures were observed in the upper layer and no presence of the intermediate plateau. On the other hand, for the faster increase of fuel supply rate (less than 1000 sec), like in Fig. 2 and Fig. 3, the temperatures were lower than 1000 °C and a plateau was observed (Fig. 5). Moreover there is a drop in the upper layer temperature when external burning starts. That decrease can be observed for the corner far away from the compartment opening. The second factor controlling the temperature distribution was the opening size (Fig. 5). For bigger opening the higher temperatures were recorded.

In addition, it was observed that there may be a correlation between the maximum smoke yield before external burning and temperature of the upper layer. This issue needs further investigation and therefore it is not discussed here.

CONCLUSIONS

The main conclusions are:
a) Carbon monoxide and smoke yields for underventilated combustion in a compartment are over one order of magnitude larger than the yields for overventilated combustion. For example, the ratio of carbon monoxide to smoke yield is constant for overventilated combustion and equals $0.34 \pm 0.05 \text{ (g/g)}$ [27], whereas it is larger by an order of magnitude during underventilated conditions before external burning occurs (2.1-13.2 for propane). Similar results were also derived in [28] for underventilated conditions before external burning (6.3 to 15.2 for hexane). Moreover, it seems that this ratio increases for higher equivalence ratio, at least for basic hydrocarbons like propane or hexane.

b) The carbon monoxide and smoke yields increase during underventilated conditions before external burning occurs. The $CO$ yield can increase by a factor of 5, whereas the smoke yield by a factor of 3 for our studies with propane (Fig. 3). The maximum value of the carbon monoxide yield can be observed just before flames appear outside; this is the same for the smoke yield.

c) The variation in the ratio of CO to smoke yield (Fig. 4) for higher equivalence ratios indicates that the carbon monoxide $CO$ and smoke yields for underventilated conditions may depend also on the temperature and residence time. This problem needs further investigation.

d) The present results for the increased amounts of carbon monoxide and smoke are applicable if, during the fire growth, underventilated conditions develop without external burning. Current engineering calculations for smoke and carbon monoxide can not predict the high concentrations of carbon monoxide and smoke measured in such a scenario. Whether these conditions can be developed will depend on whether the gas temperatures in the front of the enclosure are able to ignite the unburned gases issuing from the enclosure as recent results indicate [30].
Fig. 5. Upper layer temperature together with HRR. 2 boxes geometry. Fuel: propane.
(a) Opening size 0.1m*0.25m. (b) Opening size 0.2m*0.2m. (c) Opening size 0.075m*0.2m.

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