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# ACCURATE CALCULATIONS OF HEAT RELEASE IN FIRES

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## <u>Abstract</u>

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In the field of reaction-to-fire test, the application of the Oxygen Consumption (OC) and Carbon Dioxide Generation (CDG) calorimetry have been used extensively both at bench-scale and in large-scale to calculate heat release rates for well-ventilated fires. Both methods, however, provide only approximate heat release rates since average values of the heat of combustion per unit mass of oxygen consumed and carbon dioxide generated are used. For the calculations of accurate heat release rates, actual elemental compositions of the materials and net heat of complete combustion values are needed. In addition, effects of large amounts of soot formed in under-ventilated fires need to be accounted for in the calculations.

This paper deals with a modification of the CDG calorimetric relationships for the generation of smoke. The soot modified CDG calorimetric relationships show that for well-ventilated fires, the soot correction is generally negligibly small, but it becomes important for under-ventilated fires.

### Introduction

Fire is often considered as the most hazardous accidental event which may affect safety in the chemical industries. The fire damage may be thermal or non thermal. As examples, the fire plume may transport a variety of toxic effluents, which may injure the staff of the industrial premises and the fire fighters, as well as the inhabitants in the neighbourhood. Intense radiation produced by big fires may cause serious burn injuries and generate "domino effects" to previously non affected equipment in the vicinity and result in related phenomena such as jetfires, fireballs, BLEVEs<sup>1</sup>. Moreover, polluted extinction waters while unconfined may greatly affect the aquatic environment. Although several ambitious projects were recently carried out in the field, there is still much work to be performed to get validated techniques capable of predicting (and keeping under acceptable control) the consequences of indoor and outdoor large chemical fires.

Heat release rate evaluation is a common practise in any fire risk assessment procedure. Usual method to measure heat release rate is based on the application of the oxygen consumption (OC) [1-4] and carbon dioxide generation (CDG) calorimetry [1]. The OC calorimetry states that heat of complete combustion per unit mass of oxygen consumed is approximately constant

<sup>&</sup>lt;sup>1</sup> Boiling Liquid Expanding Vapour Explosions

for many carbon and hydrogen containing organic solids, liquids and gaseous compounds [3,5]. Hugget [3] found an average value of the heat of combustion to be 13.1 kJ per gram of oxygen consumed with a  $\pm$  5% variation. For a large number of liquids, gases, and solids, Tewarson [1] found the average value to be 12.8 kJ per gram of oxygen consumed with a  $\pm$  7% variation. đ,

Our contribution specifically focuses on CDG calorimetry that similarly states that heat of complete combustion per unit mass of carbon dioxide generated is approximately constant for most organic liquids and gaseous compounds and for many organic solids [1]. The heat of combustion per unit mass of carbon dioxide generated for a large number of gases, liquids and solids is 13.3 kJ/g with a  $\pm$  11% variation. Since oxygen is a reactant and carbon dioxide is a product, the heat release rates from OC and CDG calorimetry are found to be similar, except for low heat release rates, where measurement accuracy of oxygen consumption becomes an important factor.

The heat release rates, calculated from OC and CDG calorimetry using average values of the heat of combustion per unit mass of oxygen consumed or carbon dioxide generated, are only approximate. For accurate heat release rate calculations, both OC and CDG calorimetry require actual elemental compositions of the materials and net heat of complete combustion needs to be measured or calculated from bond energies and heats of formation.

Heat release rate calculations for under-ventilated fires also need to be improved if large amounts of soot are released in addition to various gaseous effluents. This paper presents a modified relationship for the CDG calorimetry to account for conversion of fuel-carbon into soot.

## **Theoretical analysis**

The OC and CDG calorimetry are implemented both at bench-scale and in large-scale reactionto-fire tests [6,7,8,9,10,11]. Since most of these tests are carried out in open systems, a hood must be placed above the experimental test rig to exhaust the products plus dilution air. Measurement of gas flow rate and temperature and composition of gases (molar fractions of oxygen, carbon dioxide and carbon monoxide) are used to calculate the heat release rate.

In the CDG calorimetry, the heat release rate is calculated from the measurement of the mass generation rate of  $CO_2$ , corrected from the mass generation rate of CO [1]:

$$\dot{q} = E_{CO_2} (\dot{m}_{CO_2} - \dot{m}_{CO_2}^0) + E'_{CO} \quad \dot{m}_{CO}$$
(1)

where

 $\dot{q} = heat release rate (kW)$   $E_{CO_2} = energy release per unit mass of CO_2 generated for complete combustion to CO_2 (kJ.kg^{-1})$   $E'_{CO} = energy release per unit mass of CO generated for incomplete combustion to CO (kJ.kg^{-1})$   $\dot{m}_{CO_2}^0 = mass flow rate of CO_2 in the incoming air (kg.s^{-1})$   $\dot{m}_{CO_2} = mass flow rate of CO_2 in the exhaust duct (kg.s^{-1})$   $\dot{m}_{CO} = mass flow rate of CO in the exhaust duct (kg.s^{-1})$ 

Where, the average value of  $E_{CO_2} = 13.3$  MJ.kg<sup>-1</sup>  $\pm 11\%$  and  $E_{CO} = 11.1$  MJ.kg<sup>-1</sup>  $\pm 18\%$ .

The 11 and 18 % variations suggest that energy produced respectively per unit mass of carbon dioxide or carbon monoxide generated is slightly more fuel dependent than the energy generated per unit mass of oxygen consumed [12]. The measurement accuracy for low heat release rates, on the other hand, is higher for the generation rates of CO and CO<sub>2</sub> than the consumption rate of O<sub>2</sub> [1].

The combustion reactions generating carbon dioxide and carbon monoxide may be written respectively as

$$C_a H_b O_c N_d + (a + \frac{b}{4} - \frac{c}{2}) O_2 \xrightarrow{E_{fuel}} a CO_2 + \frac{b}{2} H_2 O + \frac{d}{2} N_2$$
 (2)

$$C_a H_b O_c N_d + \left(\frac{a-c}{2} - \frac{b}{4}\right) O_2 \xrightarrow{E'_{fuel}} a CO + \frac{b}{2} H_2 O + \frac{d}{2} N_2$$
(3)

where,

 $E_{fuel}$  = energy release per unit mass of fuel consumed for complete combustion (kJ.kg<sup>-1</sup>)  $E'_{fuel}$  = energy release per unit mass of fuel consumed for incomplete combustion to CO (kJ.kg<sup>-1</sup>)

As the value of energy release  $E_{fuel}$  is known for complete combustion of the fuel, the energy release  $E_{co}$ , follows from

$$E_{CO_2} = E_{fuel} \frac{M_{fuel}}{a M_{CO_2}} \tag{4}$$

where,

 $M_{fuel} = molecular weight of fuel (kg.kmol<sup>-1</sup>)$   $M_{CO_2} = molecular weight of CO_2 (44 kg.kmol<sup>-1</sup>)$ a = number of carbon atom in the molecular structure of the burning fuel

According to Hess law and considering the oxidation reaction of carbon monoxide to carbon dioxide

$$CO + \frac{1}{2}O_2 \xrightarrow{\Delta H_{CO}} CO_2 \tag{5}$$

the energy  $E'_{CO}$  follows from

$$E'_{CO} = \left(E_{fuel} \frac{M_{fuel}}{a M_{CO}} - \Delta H_{CO}\right)$$
(6)

where

 $\Delta H_{co}$  = energy release per unit mass of CO consumed for the burning of CO (10.1 MJ.kg<sup>-1</sup> CO)  $M_{co}$  = molecular weight of CO (28 kg.kmol<sup>-1</sup>)

Since the water vapour is removed from the sampling line before the measurement of  $O_2$ ,  $CO_2$  and CO molar fractions, the mass flow rate of  $CO_2$  in the incoming air follows from

$$\frac{\dot{m}_{CO_2}^o}{M_{CO_2}} = \frac{\dot{m}_a}{M_a} (l - Y_{H_2O}^0) Y_{CO_2}^{A^0}$$
(7)

where

 $\dot{m}_{a} = mass flow rate of the incoming air (kg.s<sup>-1</sup>)$  $M_{a} = molar weight of the incoming air (kg.s<sup>-1</sup>)$  $Y_{H_{2}O}^{0} = molar fraction of water vapour in the incoming air$ 

# $Y_{CO_1}^{A^0}$ = measured<sup>2</sup> molar fraction of carbon dioxide in the incoming air

The mass flow rates of CO<sub>2</sub> and CO in the exhaust duct are given respectively by

$$\frac{m_{CO_2}}{M_{CO_2}} = \frac{\dot{m}_e}{M_e} (I - Y_{H_2O}) Y_{CO_2}^A$$
(8)

$$\frac{\dot{m}_{CO}}{M_{CO}} = \frac{\dot{m}_{e}}{M_{e}} (I - Y_{H_{2O}}) Y_{CO}^{A}$$
(9)

where

$$\begin{split} \dot{m}_{e} &= mass \ flow \ rate \ in \ the \ exhaust \ stack \ (kg.s^{-1}) \\ M_{e} &= molar \ weight \ of \ the \ gas \ in \ the \ exhaust \ stack \ (kg.s^{-1}) \\ Y_{H_{2O}} &= molar \ fraction \ of \ water \ vapour \ in \ the \ exhaust \ flow \\ Y_{CO_{2}}^{A} \ Y_{CO}^{A} &= measured \ molar \ fraction \ of \ CO_{2} \ and \ CO \ respectively \ (during \ the \ combustion \ test) \end{split}$$

Lastly, the resulting equation to calculate heat release rate by CDG calorimetry is given by

$$\dot{q} = \frac{\dot{m}_{e}}{M_{e}} (I - Y_{H_{2}O}) (E_{CO_{2}} Y_{CO_{2}}^{A} M_{CO_{2}} + E'_{CO} Y_{CO}^{A} M_{CO}) - \frac{\dot{m}_{a}}{M_{a}} (I - Y_{H_{2}O}^{0}) Y_{CO_{2}}^{A^{0}}$$
(10)

The molar fraction of water vapour in the exhaust stack is rarely measured because water vapour is in most cases removed before the gas stream is analysed. However, using the water vapour molar balance (11), the conservation of the mass flow of nitrogen<sup>3</sup> (2) and the algebraic expression of the molecular weight of the exhaust gas (12), one may obtain a solvable system of three equations with three unknowns  $(Y_{H_2O}, M_e \text{ and } \dot{m}_a)$ :

$$Y_{H_2O} \frac{\dot{m}_e}{M_e} = Y_{H_2O}^0 \frac{\dot{m}_a}{M_a} + \left(\frac{\dot{m}_{CO_2} - \dot{m}_{CO_2}^0}{M_{CO_2}} + \frac{\dot{m}_{CO}}{M_{CO}}\right) \frac{b}{2a}$$
(11)

$$\dot{m}_{a} = \frac{(I - Y_{H_{2O}}) (I - Y_{CO_{2}}^{A} - Y_{CO}^{A} - Y_{O_{2}}^{A})}{(I - Y_{H_{2O}}^{0}) (I - Y_{O_{2}}^{A^{0}} - Y_{CO_{2}}^{A^{0}})} \frac{M_{a}}{M_{e}} \dot{m}_{e}$$
(12)

$$M_{e} = M_{O_{2}}Y_{O_{2}} + M_{CO_{2}}Y_{CO_{2}} + M_{CO}Y_{CO} + M_{H_{2}O}Y_{H_{2}O} + (I - Y_{O_{2}} - Y_{CO_{2}} - Y_{CO} - Y_{H_{2}O})M_{N_{2}}$$
(13)

with,

$$Y_i = Y_i^A (I - Y_{H,O})$$
 i:  $O_2$ ,  $CO_2$  and  $CO$  (14)

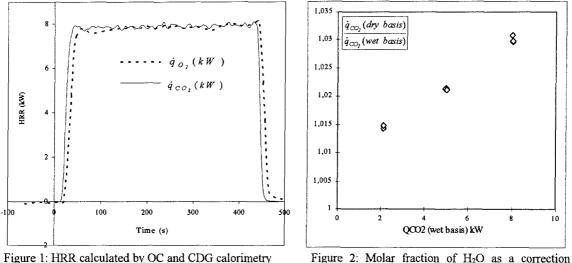
Due to the large dilution factor of the combustion gases by the air entrained into the exhaust hood, it can generally be assumed that  $M_e$  is nearly equal to  $M_a$ .

<sup>&</sup>lt;sup>2</sup> The nomenclature is the same as that used by Janssens [12]. The superscript A refers to mole fraction of any species (except  $H_2O$  and soot) measured in the analyser (which is different from the corresponding molar fraction in the exhaust flow).

 $<sup>^{3}</sup>$  It is assumed that N<sub>2</sub> does not participate in the oxidation reactions because temperatures in fires are usually too low to allow high production of nitrogen oxides.

### **Basic experimental validation at INERIS**

Experiments were performed with gas burner at bench-scale (at INERIS, France) by use of a fire calorimeter derived from both the FMRC 50 kW flammability apparatus [1] and the Rhône-Poulenc test-rig [13]. The gas burner was fed with a constant mass flow rate of methane as fuel. The mass flow rate of diluted fire gases in the exhaust duct was regulated to a value of 100 kg.h<sup>-1</sup>. The measurements were made for O<sub>2</sub>, CO<sub>2</sub>, CO and unburned hydrocarbons molar fractions in the exhaust duct, the ambient air moisture and the volumetric flow rate of gases in the exhaust duct. As expected for all the experiments, the carbon monoxide and unburned hydrocarbons molar fractions were negligible. Figure 1 shows the heat release rates calculated from the OC calorimetry  $\dot{q}_{O_2}$  according to Janssens's formulae [12] on a wet basis (with ambient air moisture correction)and the CDG calorimetry  $\dot{q}_{CO_2}$  according to equation (10) also on a wet basis (with water vapour correction). As expected, the curves show that both calculation methods are in perfect agreement.



(burning product =  $CH_4$ )

Figure 2: Molar fraction of  $H_2O$  as a correction factor in HRR calculation (burning product =  $CH_4$ )

Further experiments were carried out with different mass flow rates of methane, to get different heat release levels with the same overall exhaust flow. The ratio of the heat release rate calculated from the CDG calorimetry on a dry basis to that calculated on a wet basis was plotted versus the latter parameter (figure 2). Figure 2 referring to these experiments, where the heat release rate has been increased within a range of 4:1, shows a very weak influence of  $Y_{H_2O}$  in terms of correcting factor of the heat release rate (3% at maximum). It comes to a conclusion that this factor is simply negligible or easily kept under control by the user, for instance by provision of adequate operating conditions in the experiments. In fact, it is a common practice to report rate on a dry basis (as it is also done when OC calorimetry is used), only by neglecting water vapour molar fractions and providing large dilution factor of the fire gases.

# <u>Effect of incomplete combustion of fuel carbon into soot on heat release rate calculation</u>

The production of soot from flaming combustion may be affected by many factors [14]. The effect of ventilation has been studied for many materials [1,15]. It has been shown that the soot production increases with restricted ventilation. The soot production also depends on the chemical nature of the material being burned. Compounds such as methyl alcohol, carbon monoxide and formaldehyde do not produce soot in significant quantities. For other compounds, under identical conditions in diffusion flames, the soot production is higher for unsaturated hydrocarbons than the corresponding saturated hydrocarbons. The general trend observed in the sooting tendency follows the order [16]

### Aromatics > alkynes > alkenes > alkanes

Another known fact is that halogen compounds accelerate the rate of soot formation.

The soot production (in term of yield) may be as high as the carbon monoxide production both for well-ventilated fires and under-ventilated fires [1,17,18]. A modified equation is thus proposed in order to take account of the soot production for application of CDG calorimetry:

$$\dot{q} = E_{CO_{2}} (\dot{m}_{CO_{2}} - \dot{m}_{CO_{2}}^{0}) + E'_{CO} \dot{m}_{CO} + E''_{S} \dot{m}_{S}$$
(15)

where

 $E''_s$  energy release per unit mass of soot generated for incomplete combustion to soot  $(kJ.kg^{-1})$  $\dot{m}_s$  mass flow rate of soot in the exhaust duct  $(kg.s^{-1})$ 

Although the soot production depends on several parameters such as the type of flame and the nature of the burning fuel, the properties of the carbon produced are little affected by these parameters [19]. Chemical analysis shows that (mature) soot particles generated from hydrocarbons burning in diffusion flames contain about 1% by weight of hydrogen and oxygen [19,20]. It can thus be assumed that soot particles are principally graphitic carbon particles. Whilst chemical processes of soot formation are very complex, the overall combustion reaction which produced soot may be written as:

$$C_a H_b O_c N_d + (\frac{b}{4} - \frac{c}{2}) O_2 \xrightarrow{E^* s} a C + \frac{b}{2} H_2 O + \frac{d}{2} N_2$$
 (16)

Considering the oxidation reaction of carbon to carbon dioxide

$$C + O_2 \xrightarrow{\Delta H_S} CO_2 \tag{17}$$

and according to the Hess law, the heat release  $E''_s$  per unit mass of carbon generated follows from:

$$E''_{s} = \left(E_{fuel} \frac{M_{fuel}}{a M_{s}} - \Delta H_{s}\right)$$
(18)

where

 $\Delta H_s$  = energy release per unit mass of carbon consumed (32.7 MJ.kg<sup>-1</sup> of C)  $M_s$  = molecular weight of carbon (12 kg.kmol<sup>-1</sup>) Since condensable species and soot particles are removed from the sampling line before measurement of  $O_2$ ,  $CO_2$  and CO molar fractions, the mass flow rates of carbon dioxide and carbon monoxide in the exhaust stack are given by:

$$\frac{m_{CO_2}}{M_{CO_2}} = \frac{\dot{m}_e}{M_e} Y_{CO_2}^A \ (l - \sum_n Y_{cond,n} - Y_S)$$
(19)

$$\frac{\dot{m}_{CO}}{M_{CO}} = \frac{\dot{m}_{e}}{M_{e}} Y_{CO}^{A} \ (l - \sum_{n} Y_{cond,n} - Y_{S})$$
(20)

where

 $Y_{cond,n}$  molar fractions of condensable species such as  $H_2O$ , acid gases (HCl,...)  $Y_s$  molar fraction of graphitic carbon

The mass flow rate of soot can be calculated from optical smoke measurements. According to Beer-Lambert law, the attenuation of monochromatic light over a given optical path through the smoke generated by the burning fuel can be expressed as

$$\frac{I}{I_0} = e^{-k.L} \tag{21}$$

where

 $I_0$  = intensity of incident light

*I* = intensity of the transmitted light through smoke

L = optical path length through smoke (m)

k = light extinction coefficient (m<sup>-1</sup>)

It has been shown that mass concentration of soot particles is proportional to the light extinction coefficient k [21,22]:

$$C_s = \frac{k}{\sigma_s} \tag{22}$$

where,

 $C_s = mass \ concentration \ of \ smoke \ particles \ (kg.m<sup>-3</sup>)$  $\sigma_s = specific \ extinction \ area \ per \ unit \ mass \ of \ soot \ (m<sup>2</sup>.kg<sup>-1</sup>)$ 

The value of the specific extinction area  $\sigma_s$  is roughly constant for fuels burning in flaming mode and producing primarily graphitic carbon soot. As an example, a practical value of this specific extinction coefficient  $\sigma_s$  has been quoted by Mulholland et al [23].

In open systems, since the attenuation of light through smoke is measured in the exhaust stack, the mass flow rate of soot follows as:

$$\dot{m}_s = C_s \ \dot{V_e} = \frac{k \ V_e}{\sigma_s} \tag{23}$$

where

 $\dot{V}_e$  = volume flow rate in the exhaust chimney at the actual temperature where the photometer is located ( $m^3.s^{-1}$ )

The molar fraction of soot in the exhaust stack can be written as

$$Y_{s} = \frac{\dot{m}_{s}}{\dot{m}_{e}} \frac{M_{e}}{M_{s}}$$
(24)

Lastly, the heat release rate calculated from CDG calorimetry is given by

$$\dot{q} = \frac{\dot{m}_{e}}{M_{e}} (1 - \sum_{n} Y_{cond,n} - Y_{S}) (E_{CO_{2}} Y_{CO_{2}}^{A} M_{CO_{2}} + E'_{CO} Y_{CO}^{A} M_{CO}) - \frac{\dot{m}_{a}}{M_{a}} (1 - Y_{H_{2}O}^{0}) Y_{CO_{2}}^{A^{0}} + E''_{S} \frac{k \dot{V}_{e}}{\sigma_{S}}$$
(25)

As in the previous case (where the production of soot is insignificant), to calculate the molar fraction of water vapour, the mass flow rate of the incoming air and the molar weight of the exhaust gas, the following system of three equations with three unknowns can be solved:

$$Y_{H_2O} \frac{\dot{m}_e}{M_e} = Y_{H_2O}^0 \frac{\dot{m}_a}{M_a} + \left(\frac{\dot{m}_{CO_2} - \dot{m}_{CO_2}^0}{M_{CO_2}} + \frac{\dot{m}_{CO}}{M_{CO}} + \frac{\dot{m}_s}{M_s}\right) \frac{b}{2a}$$
(26)

$$\dot{m}_{a} = \frac{(l - Y_{O_{2}} - Y_{CO_{2}} - Y_{CO} - \sum_{n} Y_{cond,n} - Y_{S})}{(l - Y_{H_{2}O}^{0}) (l - Y_{O_{2}}^{A^{0}} - Y_{CO_{2}}^{A^{0}})} \frac{M_{a}}{M_{e}} \dot{m}_{e}$$
(27)

$$M_{e} = M_{O_{2}}Y_{O_{2}} + M_{CO_{2}}Y_{CO_{2}} + M_{CO}Y_{CO} + \sum_{n}M_{cond,n}Y_{cond,n} + M_{S}Y_{S} + Y_{N_{2}}M_{N_{2}}$$
(28)

with,

$$Y_i = Y_i^A \left( l - \sum_n Y_{cond,n} - Y_s \right) \qquad i: O_2, CO_2 \text{ and } CO$$
(29)

$$Y_{N_2} = (l - Y_{O_2} - Y_{CO_2} - Y_{CO} - \sum_n Y_{cond,n} - Y_S)$$
(30)

## Discussion at the light of experimental results from Tewarson

A first assessment of the relevancy of such a modified equation for the calculation of heat release rate by CDG calorimetry has been studied using experimental data of Tewarson [24]. Generalised correlation between yields of combustion products and equivalence ratio have been established by Tewarson for polymers:

$$f_{i,vc} = f_{i,wv} \left( 1 + \frac{\alpha}{\exp(\beta \ \Phi^{-\xi})} \right)$$
(31)

where,

 $f_{i,vc}$  = yield of i for ventilation-controlled fires (gram of i produced per gram of burned fuel)  $f_{i,wv}$  = yield of i for well-ventilated fires (gram of i produced per gram of burned fuel)  $\Phi$  = equivalence ratio  $\alpha$ ,  $\beta$ ,  $\xi$  = correlation coefficients

The equivalence ratio is a parameter which characterises the degree of ventilation in reaction-to-fire test. For polymers such as polyethylene (PE) and polystyrene (PS), the values of  $f_{i,wv}$ ,  $\alpha$ ,  $\beta$  and  $\xi$  are listed in table 1.

	$f_{i,wv}$	α	β	ξ
$CO_2$ (PE)	2.76	-1	2.5	1.2
CO (PE)	0.024	26	2.5	2.8
Soot (PE)	0.06	2.2	2.5	1
CO <sub>2</sub> (PS)	2.33	-1	2.5	1.2
CO (PS)	0.06	2	2.5	2.5
Soot (PS)	0.164	2.8	2.5	1.3

Table 1: Correlation coefficients to account for the effects of ventilation on the generation rate of  $CO_2$ , CO and soot, from Tewarson [24].

Since the yield of product i may be defined as

$$f_{i,vc} = \frac{\dot{m}_i - \dot{m}_i^0}{\dot{m}_f}$$
(32)

the heat release rate (according to equation 15) may be written as

$$\dot{q} = \dot{m}_{f} \left( f_{CO_{2},vc} E_{CO_{2}} + f_{CO,vc} E'_{CO} + f_{S,vc} E''_{S} \right)$$
(33)

where,

 $\dot{m}_f$  = mass loss rate of the fuel (kg.s<sup>-1</sup>)

To assess the influence of soot production on the heat release rate calculation, the ratio (equation 34) of the heat release rate calculated by the carbon dioxide generation principle (without soot correction) to the heat release rate corrected for the soot generation has been plotted versus equivalence ratio (figure 3):

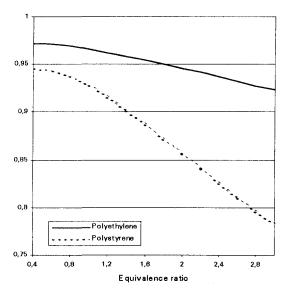


Figure 3: Influence of soot production on heat release rate calculation by CDG Calorimetry.

$$\frac{\dot{q}_{CO_2+CO}(kW)}{\dot{q}_{CO_2+CO+S}(kW)} = \frac{f_{CO_2,vc}E_{CO_2} + f_{CO,vc}E'_{CO}}{f_{CO_2,vc}E_{CO_2} + f_{CO,vc}E'_{CO} + f_{S,vc}E''_{S}}$$
(34)

As it can be seen from figure 3, in wellventilated fire conditions. the correction accounting for soot generation on the heat release rate calculation is negligible in both examples given (PE and PS). On the other hand, in under-ventilated fire conditions, the situation moves. The higher is the equivalence ratio (e.g. the lower is the fire ventilated), the higher is the underestimation of the heat release rate, if the contribution of soot keeps neglected. The real significance of this underestimation in practical application is influenced by the nature of the tested material.

# **Conclusion**

CDG calorimetry is a useful method to calculate heat release in fires. For accurate heat release rate calculations, molecular compositions of the materials are needed as in any other practical method. If the molecular composition of the material being burned is known, the water vapour molar fraction in the exhaust stack can be calculated to improve the measurement of the heat release rate by CDG calorimetry if required. The sooting tendency of materials is another important consideration for accurate calculations of heat release. A modified equation applying for CDG calorimetry has been proposed and shortly discussed in terms of relevancy, especially for ventilation-controlled fires.

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# **Nomenclature**

- *a* Stoichiometric coefficient for carbon
- *b* Stoichiometric coefficient for hydrogen
- *c* Stoichiometric coefficient for oxygen
- d Stoichiometric coefficient for nitrogen
- $E_{fuel}$  Energy release per unit mass of fuel burned for complete combustion (kJ.kg<sup>-1</sup>)
- $E_{CO_1}$  Energy release per unit mass of CO<sub>2</sub> produced for complete combustion to CO2 (kJ.kg<sup>-1</sup>)
- $E'_{CO}$  Energy release per unit mass of CO produced for incomplete combustion to CO (kJ.kg<sup>-1</sup>)
- $E''_s$  Energy release per unit mass of carbon produced for incomplete combustion to graphitic carbon (kJ.kg<sup>-1</sup>)
- $f_i$  Yield of i (gram of i produced per gram of burned fuel)
- *I*<sub>0</sub> Intensity of incident light
- *I* Intensity of the transmitted light through smoke
- k Light extinction coefficient  $(m^{-1})$
- L Optical path length through smoke (m)
- $\dot{m}$  Mass flow rate (kg.s<sup>-1</sup>)
- M Molecular weight (kg.kmol<sup>-1</sup>)
- $\dot{q}$  Heat Release Rate (kW)
- $\dot{V}_{a}$  Volume flow rate in the exhaust duct (m<sup>3</sup>.s<sup>-1</sup>)
- Y Molar fraction
- $\Delta H_{co}$  Energy release per unit mass of CO consumed in the burning of CO (kJ.kg<sup>-1</sup>)
- $\Delta H_s$  Energy release per unit mass of carbon consumed in the burning of carbon (kJ.kg<sup>-1</sup>)
- $\alpha \beta \xi$  Correlation coefficients
- $\sigma_s$  Specific extinction area per unit mass of soot (m<sup>2</sup>.kg<sup>-1</sup>)
- $\Phi$  Equivalence ratio

## **Subscripts**

- *a* Refers to incoming air
- *e* Refers to gases in the exhaust stack

- Refers to burning fuel f
- Ventilation-controlled tires VC
- Well-ventilated fires wv

### **Superscripts**

- Refers to molar fractions in the analyser A
- Â<sup>0</sup> Refers to molar fractions in the analyser prior to the test
- 0 Refers to incoming air

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