



Ability of the Fire Propagation Apparatus to characterise the heat release rate of energetic materials

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ABSTRACT

Energetic materials encompass a wide range of chemical compounds. They react very rapidly releasing large amounts of energy. One of their peculiarities is that they carry an oxidizer and do not require oxygen from the air as their primary reaction partner. The aim of this paper is to present an analysis of the ability to estimate the heat release rate of a sample energetic material using two calorimetric methodologies. The methods are based on Oxygen Consumption and Carbon Dioxide Generation principles. Data have been obtained from experiments carried out with the Fire Propagation Apparatus. First, results from smoke powder combustion tests reveal significant discrepancies between the two approaches. Results from a sensitivity analysis realised in a previous work underlined that the most likely parameters to alter the heat release rate estimation are the energy constants and the concentration of oxygen. Correction procedures have been developed; one based on the estimation of the amount of oxygen supplied by the oxidizer, and a second one based on the calculation of new energy constants accounting for the chemical decomposition of the tested materials. Results are presented in this study.

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1. Introduction

Understanding the thermal and chemical impact of burning energetic materials in both normal use and accidental scenarios is becoming increasingly relevant [1]. Energetic materials encompass a wide range of chemical compounds. They include materials storing a high level of chemical energy such as explosives, propellants, pyrotechnics and unsteady chemicals. The behaviour of these materials in the event of an explosion (e.g. deflagration or detonation) is relatively well-known; however fundamental scientific questions are still unanswered on the mechanisms of heat release when slower reactions prevail. Moreover, energetic materials often contain harmful substances whose origin and fate is many times unknown. Thus, in the case of a fire, it is still not possible to predict the toxicity of the generated products and the amount of heat released.

Heat release rate (HRR) is one of the most important variables for characterising a fire [2] since most variables associated to tenability can be linked to the HRR. The first standard method for measuring heat release rates in room fires dates from 1982 and

since then, bench scale techniques have been developed for this purpose. The most widely used is the Cone Calorimeter [3,4], which was designed to measure simultaneously the heat release rate, time of ignition, burning rate, smoke production, CO₂, CO and O₂ concentrations. The principles of the Cone Calorimeter have been extended to study flammability parameters for polymers, standard “fire” fuels and many chemicals [5] by using the FM-Global Fire Propagation Apparatus (FPA) [6]. The main advantage of the FPA over the Cone Calorimeter is that the combustion region is physically delimited by an infrared transparent quartz tube; thus, the incoming flow can be adjusted in order to simulate both under ventilated and well ventilated conditions (i.e. atmosphere poor or rich in O₂).

The main method used to calculate the HRR from the FPA tests is oxygen consumption (OC) calorimetry, nevertheless an alternate method, carbon dioxide generation (CDG) calorimetry can also be used. Both methodologies are intimately linked together and rely on a species evolution concept that is easier to apply than the thermal balance required by other standard tests such as the OSU calorimeter [7].

These techniques state that in fires the amount of energy released per unit of oxygen consumed (in case of OC) or per unit of carbon dioxide generated (if CDG considered) is approximately constant. This assessment has been validated for a large number of fuels (organic liquids, gases or solids) and polymers but questions remain regarding substances such as energetic materials. The

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Nomenclature

A	cross-sectional area of the exhaust duct (m ²)
E	energy release per unit mass (kJ/kg)
K	pitot tube coefficient
\dot{m}	mass flow rate (kg s ⁻¹)
M	molecular weight (g mol ⁻¹)
ΔP	pressure drop in the Pitot tube (Pa)
\dot{q}	heat release rate (kW)
T	temperature (K)
X	molar fraction

Greek letters

ρ	density (kg m ⁻³)
ΔH_c	heat of combustion (kJ mol ⁻¹)
ψ	stoichiometric yield

Subscripts

a	incoming gas
e	exhaust gas

Superscript

A	measured analyzer value
o	initial value

unifying feature of energetic materials is that they carry an oxidizer [8] therefore, a significant amount of O₂ consumed during the reaction may be directly supplied by the material itself. This quantity, if neglected or miscalculated, could affect HRR estimations.

The aim of this work is to study the applicability of general calorimetric equations when energetic materials like a smoke powder (a mixture of ingredients designed to release obscuring smoke flow) is burned and study their validity in order to assess the ability of the FPA (or other fire calorimeters) to thermally characterise this type of compounds. Considering usual assumptions for OC and CDG calorimetry, results obtained with the two methods have been compared and a sensitivity analysis of the HRR calculations has been carried out in order to identify the main parameters likely to raise variations in the results.

2. Heat release measurement methodology

Any burning material generates heat. In case of energetic materials, it is likely that it comes along with smoke but also toxic gases and vapours [9]. Depending on the size of the fire (i.e. the amount of energy released), different scenarios may occur [10]. Thus, the knowledge of the heat release rate of a burning material is essential in order to characterise a fire hazard. Furthermore, the production of smoke particles and toxic gases can be directly linked to this parameter [2]. Different techniques have been developed to evaluate the HRR. The simplest technique is based on direct fuel mass loss measurements and an assumed heat of combustion [11]. If the heat of combustion of the material is known [12], a good estimation of the HRR can be determined from the following expression:

$$\dot{q}_{\text{mass loss}} = \Delta H_c \dot{m}_{\text{fuel}} \quad (1)$$

For conditions close to complete combustion, the uncertainty on the HRR estimation is less than 10% [13]. In case of incomplete combustion the accuracy decreases. Non-negligible amounts of CO and soot will be generated. The generation of one mole of CO or soot releases less energy than the production of one mole of CO₂. Finally, the heat of reaction is lower than ΔH_c and Eq. (1) could lead to a significant overestimation of the HRR. A correction for ΔH_c can be applied [11] but it implies detailed understanding of the

decomposition chemistry. The mass loss principle has the potential to provide relevant outcomes but it is strictly dependent on the knowledge of the heat of combustion of the material. The heat of combustion is unfortunately not always available.

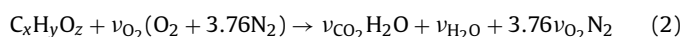
Another way to estimate the HRR is by conducting an energy balance between the heat released by the burning material and the rise of enthalpy (temperature) of the mass flow of air and combustion products through the exhaust duct of the apparatus [6]. A major issue impacting uncertainty of the method is the evaluation of the heat losses. Smith proposed an expression to account for the transient heat exchange between the air stream and the calorimeter apparatus which entails significant additional temperature measurements and several calibration factors [14]. It nevertheless demonstrated good agreement with other HRR calculation methods [15].

The limitation of the mass loss approach and the complexity of estimating accurately the heat losses of the energy conservation methods encouraged researchers to develop a methodology based on species conservation. The potential use of any method to establish the HRR needs to be assessed on the basis of a comparison between the potential errors embedded in the methodology. These errors have been carefully estimated for the mass loss [11] and the energy conservation [14,15] methods but not for the species conservation approach.

2.1. Species evolution approach: theoretical principle

Species evolution approach has been defined from Thornton's principle [16]. In 1917, Thornton established that for a large number of organic liquids and gases, the amount of energy released by a burning material for a complete combustion was proportional to the amount of O₂ consumed by the reaction. Later in the 70 s, Tewarson developed a similar statement based this time on the generation of CO₂ [17]. It is of interest to compare these observations with the HRR calculation based on mass loss presented earlier. Given Eq. (1), HRR is proportional to the amount of fuel burnt, the proportional coefficient being ΔH_c . As shown in Fig. 1, the relation between the three parameters, fuel burning rate, consumption of O₂ and production of CO₂ is the chemistry.

The reaction of complete combustion for a chemical C_xH_yO_z is given by,



The relations between the fuel burning rate, the O₂ consumption and the CO₂ generation is given by,

$$\dot{m}_{\text{fuel}} = \frac{\Delta \dot{m}_{O_2} M_{\text{fuel}}}{\nu_{O_2} M_{O_2}} \quad (3)$$

$$\dot{m}_{\text{fuel}} = \frac{\Delta \dot{m}_{CO_2} M_{\text{fuel}}}{\nu_{CO_2} M_{CO_2}} \quad (4)$$

Eq. (1) can be rewritten using expressions (3) and (4),

$$\dot{q} = E_{O_2} \Delta \dot{m}_{O_2} = E_{O_2} (\dot{m}_{O_2}^o - \dot{m}_{O_2}) \quad (5)$$

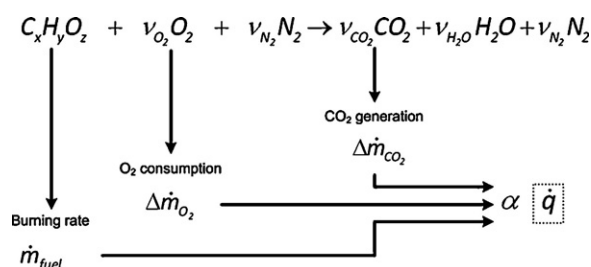


Fig. 1. Relation between mass loss, O₂ consumption, CO₂ generation and HRR.

Table 1
Energy constants estimations from Huggett [19] and Tewarson [17].

OC calorimetry	CDG calorimetry
\bar{E}_{O_2} (kJ g ⁻¹ of O ₂)	\bar{E}_{CO_2} (kJ g ⁻¹ of CO ₂)
13.1 (±5%) (Huggett [19])	13.3 (±11%) (Tewarson [17])

with

$$E_{O_2} = \frac{\Delta H_c M_{fuel}}{\nu_{O_2} M_{O_2}} \quad (6)$$

and

$$\dot{q} = E_{CO_2} \Delta \dot{m}_{CO_2} = E_{CO_2} (\dot{m}_{CO_2} - \dot{m}_{CO_2}^o) \quad (7)$$

with

$$E_{CO_2} = \frac{\Delta H_c M_{fuel}}{\nu_{CO_2} M_{CO_2}} \quad (8)$$

where $\dot{m}_{O_2}^o$ ($\dot{m}_{CO_2}^o$) represents the mass flow rate of O₂ (CO₂) from the entrained air. The latter can be defined as the air flowing through the exhaust duct when no combustion occurs. Eqs. (5) and (7) verify Thornton and Tewarson statements. A dimension analysis of coefficients E_{O_2} and E_{CO_2} shows that they characterise the amount of energy release per unit mass, respectively, of O₂ consumed and CO₂ generated. They are defined as energy constants. For a given fuel, one mole of O₂ consumed (or CO₂ produced) releases a certain amount of energy. Eqs. (5) and (7) are the base of the calorimetric methodology and are respectively referred as oxygen consumption calorimetry (OC) [18] and carbon dioxide generation calorimetry (CDG) [17].

The basic hypotheses to estimate HRR hinge on the knowledge of the energy constants and the evolution of the combustion gases concentration. The reason why these two techniques became widely used for HRR evaluation (especially the OC calorimetry) stems from the assumption that for a large number of organic solids, liquids and gaseous compounds, values found for E_{O_2} and E_{CO_2} appear to be approximately constant. Huggett [19] and Tewarson [17] determined averaged energy constants (cf. Table 1). They underline that the process occurring during the combustion of these materials is the breaking of C–C, C–H and O=O bonds which requires approximately the same amount of energy and the formation of C=O and O–H bonds which releases heat.

The main advantage of OC and CDG compared to a mass loss approach is that they allow calculating the HRR even when detailed chemistry of the materials of interest is unknown.

The only basic requirements end up to be accurate evaluations of the O₂ consumption or the CO₂ production depending on the method used. They can be performed by collecting all gases through an exhaust duct once homogeneous mixing is achieved. Apparatuses such as the Cone Calorimeter, developed in NIST by Babrauskas [3,4] or the FM–Global Fire Propagation Apparatus (FPA) [6] developed by Tewarson have been specially designed to allow these measurements. The FPA has been selected for the current study as presenting several significant advantages according to the peculiarity of energetic materials. However, the measurement procedure for both calorimeters is similar. Fig. 2 represents a schematic of the FPA fire calorimeter. A hood system topped the “reaction zone”. It has been dimensioned so that all the combustion gases are sucked up. From the hood, the system narrows to an exhaust duct to ensure gases mixing. Further down, volumetric flow rate is measured by a Pitot tube and gas sampling is operated. Gases pass through a soot filter and a cold trap. They are continuously distributed to a set of different analysers. The O₂ concentration is estimated through a paramagnetic analyser while CO/CO₂ concentrations are determined using an infrared technology. Adding instrumentation for measuring CO, Total unburned hydrocarbon

(THC) and soot enable to improve the accuracy of the results [20]. As regards the THC measure, a flame ionization detector (FID) device is used. A laser beam at $\lambda = 632$ nm is projected along the exhaust duct in order to evaluate the extinction and the smoke molar fraction.

2.2. Calorimetric equations

It has to be emphasized that the relevance of the results highly depends on the precision of the concentration measurements and the validity of several simplifying assumptions. First, all gases are considered to behave as ideal gases. Experiments presented in this study were conducted at atmospheric pressure making this assumption valid. Entrained air is only considered as N₂, O₂, CO₂, and H₂O. All other gases are accounted inert and regarded as N₂.

Species mass flow rates (\dot{m}_{O_2} , \dot{m}_{CO_2} , etc.) cannot be measured directly. They are determined from species molar fractions and the exhaust flow rate \dot{V}_e using the following expression,

$$\text{For a species } i, \quad \dot{m}_i = \frac{X_i M_i}{M_e} \dot{m}_e \quad (9)$$

where

$$X_i = (1 - X_{H_2O}) X_i^A \quad (10)$$

and

$$\dot{m}_e = \rho_e \dot{V}_e \quad (11)$$

Prior to measurement, exhaust gases are dried. Water vapour has been condensed. Species molar fractions are written according to Eq. (10). The exhaust mass flow rate is given by Eq. (11). During the reaction, combustion gases will be produced and a part of O₂ from the air entrained will be consumed. Considering reaction (2), for each mole of fuel burnt, ν_{O_2} moles of O₂ are consumed while $\nu_{CO_2} + \nu_{H_2O}$ moles of combustion gases are generated. There is a chemical expansion due to the reaction, which implies that exhaust mass flow rate, \dot{m}_e and incoming mass flow rate (entrained air), \dot{m}_a are two different parameters. Finally, species consumption (or generation) is given by,

$$\Delta \dot{m}_i = \left| \dot{m}_i - \dot{m}_i^o \right| = \left| \frac{X_i M_i}{M_e} \dot{m}_e - \frac{X_i^o M_i}{M_a} \dot{m}_a \right| \quad (12)$$

It can be assumed that, due to the combustion, the exhaust mass flow rate corresponds to the entrained air a part of which has been depleted of its O₂ and replaced by an equal or larger number of moles of combustion products [20]. The relation between \dot{m}_e and \dot{m}_a can be written as,

$$\frac{\dot{m}_e}{M_e} = \frac{\dot{m}_a}{M_a} - \frac{\Delta \dot{m}_{O_2}}{M_{O_2}} + \beta \frac{\Delta \dot{m}_{O_2}}{M_{O_2}} \quad (13)$$

with

$$\beta = \frac{\sum \nu_{products}}{\nu_{O_2}} \quad (14)$$

The depletion factor ϕ , and the expansion factor, α are introduced. ϕ is the fraction of the entrained air that is fully depleted of its oxygen during the combustion process and is given by the expression [18]:

$$\phi = \frac{\dot{m}_{O_2}^o - \dot{m}_{O_2}}{\dot{m}_{O_2}^o} \quad (15)$$

The expansion factor α , is defined as follow [18],

$$\alpha = 1 + X_{O_2} (\beta - 1) \quad (16)$$

Expressions (15) and (16) allow rewriting Eq. (13) as follow,

$$\dot{m}_e = \dot{m}_a \frac{M_e}{M_a} (1 + \phi(\alpha - 1)) \quad (17)$$

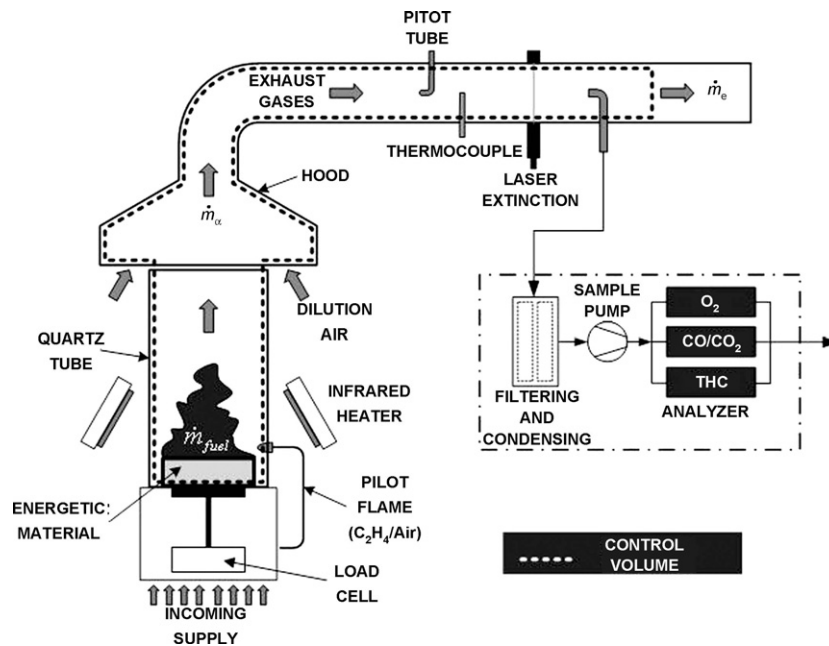


Fig. 2. Schematic view of the FM-global fire propagation apparatus with a diagram of the gas sampling system.

However, because β cannot always be estimated, the mass flow rate of air entrained can also be calculated based on the assumption of N₂ conservation [20]. Janssens defined the following expression,

$$\frac{\dot{m}_a}{M_a} = \frac{\dot{m}_e (1 - X_{H_2O})(1 - X_{O_2}^A - X_{CO_2}^A - X_{CO}^A)}{(1 - X_{H_2O}^0)(1 - X_{O_2}^0 - X_{CO_2}^0)} \quad (18)$$

The water vapour molar fraction appears in most of the equations (everyone including species concentration terms). It can be measured by means of an infrared analyser. Otherwise, X_{H₂O} produced during combustion is not considered in the calculation (i.e. X_{H₂O} = X_{H₂O}⁰).

From Eqs. (5) and (7), considering the different assumptions presented previously, Parker [18] and Janssens [20] provide complete expressions to estimate the HRR.

$$\dot{q}_{oc} = \left[E_0 \phi - (E_{O_2(CO \rightarrow CO_2)} - E_{O_2}) \left(\frac{1 - \phi}{2} \right) \frac{X_{CO}^A}{X_{O_2}^A} \right] \times X_{O_2}^A (1 - X_{H_2O}) \frac{M_{O_2}}{M_e} \frac{\dot{m}_e}{1 + \phi(\alpha - 1)} \quad (19)$$

$$\dot{q}_{CDG} = \frac{\dot{m}_e}{M_e} (1 - X_{H_2O})(E_{CO} X_{CO}^A M_{CO} + E_{CO} X_{CO}^A M_{CO}) - \frac{\dot{m}_a}{M_a} (1 - X_{H_2O}^0) E_{CO} X_{CO}^0 M_{CO} \quad (20)$$

Eqs. (19) and (20) include correction terms accounting for incomplete combustion by integrating the CO production [17,20].

Both methods have shown their ability to predict HRR accurately for standard fuels, polymers or chemicals [5]. However, the calculations involve several assumptions and various parameters susceptible to lead to the propagation of uncertainties. Combining the two principles, may present noticeable interests. For defined test conditions, convergence of HRR methods can highlight the consistency of the calorimetric methodology. Inversely, divergence of the results would underline that at least one of the calculation assumptions is not valid. It is necessary to assess this last statement when burning elements presenting peculiarity such as energetic

materials and evaluate the ability of calorimetric equations and FPA data to correctly estimate their HRR.

2.3. Application to energetic materials

The common basis of these compounds is that they contain an oxidizer in a condensed phase and thus do not require oxygen from the air as their primary reaction partner to achieve combustion [8]. Gaseous oxygen or other oxidant compounds are released during the decomposition of the oxidizer (e.g. nitrates or chlorates) initiated by an energy flux (e.g. in fire scenarios). They diffuse through the gaseous medium of the volatiles (cf. Fig. 3). It may happen that the oxidizer supplying the reaction is not sufficient for complete combustion; subsequently oxidation processes may complete making use of both material oxidizer carrier and atmospheric oxygen. Fires involving energetic materials clearly differ from conventional ones. First, the specificity of the chemistry leads to very complex reactions. On the other hand, it has been recognised that the combustion of this type of materials often goes along with high emissions of toxics [21].

It has been shown that resulting level of toxicity and HRR present degrees of correlation [2]. Then, being able to estimate the heat release variable in the case of energetic materials would be of great interest allowing essential prediction on the tenability of a space. The question in this study is to know if data obtained from the FPA

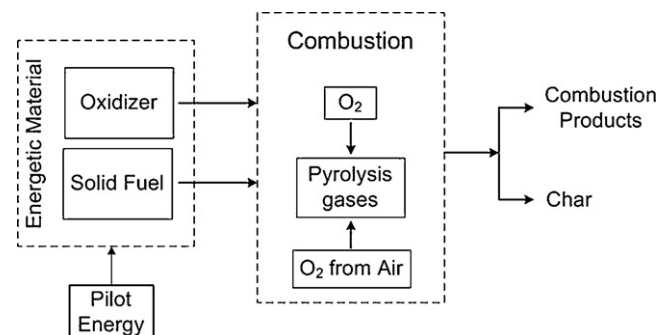


Fig. 3. Scheme of a decomposition process for energetic materials.

Table 2
Composition in mass percentage of tested smoke powders.

Components	Smoke powder 1	Smoke powder 2
Starch (C ₆ H ₁₀ O ₅)	30%	25%
Lactose (C ₁₂ H ₂₂ O ₁₁)	30%	25%
KNO ₃	40%	50%

integrated into calorimetric equations are able to provide correct evaluation of the HRR for energetic materials. It has already been noticed that OC calorimetry relies on the accurate assessment of the amount of oxygen consumed during the combustion. The peculiarity of energetic materials to react with their own oxidant, not accounted in the calculation, instead of the oxygen from air could then affect the significance of the HRR calculation. Comparing OC and CDG could contribute investigating this hypothesis. It could also highlight that one of the simplifying assumptions made be no longer valid when burning these non-standard materials.

3. Experimental setup

Combustion tests have been carried out on smoke powders. The ones used in this study consist of ternary mixtures of lactose and starch as fuel components and potassium nitrate as oxidizer. Such products are used by fire brigades in France and Switzerland in order to check the efficiency of smoke venting systems in buildings. They represent a standard type of energetic materials. Their characteristics are presented in Table 2.

As mentioned earlier, experiments have been conducted using the FM-Global Fire Propagation Apparatus. This fire calorimeter (cf. Fig. 2) comprises two main sections: the combustion line and the exhaust products (combustion gases, soot, etc.) collecting and measurement line that has been described in the previous section [6]. The material submitted to a test is placed on a sample holder mounted on a load cell and enclosed in a quartz tube restricting the combustion area. Four infrared heaters fixed at the exterior of the quartz tube allows for applying a given external heat flux onto the sample. The heating system is both air and water cooled due to the high temperatures developed by the lamps. When self ignition is not expected, ignition of the material usually occurs by use of an ethylene/air pilot flame. The FPA was instrumented with O₂, CO/CO₂ and THC analysers.

For the purpose of the study, no external heat was applied. Quartz tube was used. Samples were ignited by means of a pilot flame of ethylene/air mixture. The exhaust flow rate was set to 160 N m³ h⁻¹ and the incoming air flow rate supplied to the sample was set to 200 L min⁻¹. Each sample weighed about 50 g. Mass loss, combustion gases emissions and O₂ consumption were recorded. Each test was repeated three times.

4. Results and discussion

Two aspects need to be investigated; the behaviour of the smoke powders while burning and the influence of the oxidizer concentration in the mixture. First observations point that materials ignite and reach sustained flaming faster with powder containing 50% KNO₃. Then, combustion occurs in two stages. After the ignition of the sample, thermal decomposition begins inside the material. Short flames appear at the reaction front only on the surface. Secondly, general ignition occurs all over the sample's surface. Larger flames develop; the volume of the sample expands (cake off process) and a significant amount of soot is generated. Differences are noticed according to the KNO₃ concentration in the mixture. The burning rate increases with the concentration of oxidizer. For the 40% KNO₃ smoke powder, the combustion reaction lasts about 100 s while it decreases to about 30 s for the 50% KNO₃ powder.

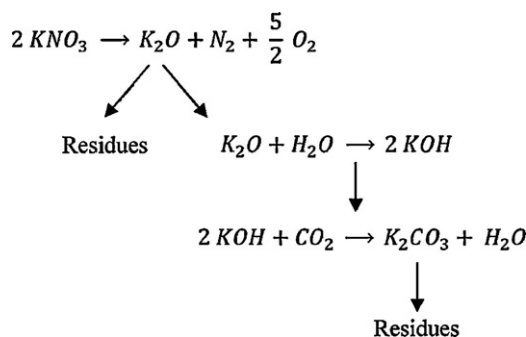


Fig. 4. Thermal decomposition of the oxidizer during the combustion.

Analysis of the residues points out the presence of char but also inorganic carbon. Further investigation based on the assumption that KNO₃ decomposes into potassium oxide (K₂O), N₂ and O₂ [22] reveals that in this case, K₂O reacts with water to form potassium hydroxide KOH. Finally, inorganic compound, potassium carbonate K₂CO₃, is produced from the reaction of KOH and CO₂ released during the combustion [23]. A mass balanced on the potassium total and the inorganic carbon confirms the hypothesis that most of the potassium degrades into potassium carbonate (cf. Fig. 4).

Regarding the emissions, the mole production rates of CO₂ and CO as well as mole consumption rate of O₂ for the combustion of a 40% KNO₃ smoke powder are plotted in Fig. 5. The combustion is incomplete, CO is significantly produced. The CO₂ mole flow rate is higher than the O₂ consumption rate. It has to be emphasized that for one mole of CO₂ generated, less than one mole of O₂ is consumed. It is different from what is usually observed with conventional fuels given that oxidizing C and H atoms requires three O atoms.

The total production of smoke is important, which is characteristic of pyrotechnics. For combustion tests carried out with the 40% KNO₃ powder, the total CO₂ production is about 21 g while the total production of CO and THC are respectively about 4 g and 0.9 g. The CO₂/CO ratio obtained is 5.25. Tests realised with the 50% KNO₃ powder present higher CO₂ levels. The total production is about 27 g while the generations of CO and THC respectively fall down to about 1.3 g and 0.15 g. The CO₂/CO ratio is nearly 21. The amount of O₂ supplied to the fuel is not enough to reach stoichiometric reaction. In terms of soot production, if optical measurement lead to equivalent results whatever powder is used, deposit of agglomerated soot particles on the quartz tube appears more important when burning the 40% KNO₃ smoke powder. Nevertheless, higher oxidizer concentration clearly leads to more complete combustion. The assumption developed in this study is that the air does not supply all the oxygen

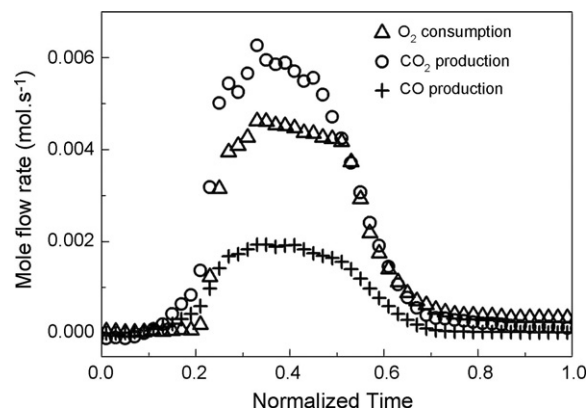


Fig. 5. Mole production rates of CO₂ and CO and mole consumption rate of O₂ during the combustion of smoke powder containing 40% KNO₃.

used during the reaction. A part of the oxidant comes from the material itself. First, it has to be noticed that lactose and starch enclose almost the same number of oxygen atoms than carbon atoms. It decreases the need in oxygen from the air required for the combustion. But furthermore, the variations of CO_2 , CO productions as well as the burning rates show that the oxidizer is a critical actor of the combustion process. Calculating the O_2 depletion for both combustion tests (40 and 50% KNO_3) highlights an excess of O_2 in the combustion products (CO_2 , CO , H_2O) compared to the amount in the fuels (starch, lactose) and the one consumed from the air. The balance in O_2 is not verified. This fact strengthens the assumption that the oxidizer is a partner of the combustion reaction and that it supplies the volatiles with a considerable quantity of O_2 . Calorimetric methodology has shown its ability to evaluate accurately HRR. However, it is interesting to analyse and compare results obtained by means of OC and CDG principles when energetic materials such as smoke powders are burned.

A comparison of calculated HRR is shown in Fig. 6. As the chemical composition of the burning material is unknown, general hypotheses introduced earlier are applied (use of the generic values \bar{E}_{O_2} and \bar{E}_{CO_2}). For identical experimental conditions, the 50% KNO_3 powder burns faster and the estimation of total energy released appears much higher. Following the assumption made on the role of the oxidizer during the combustion process, if a higher O_2 concentration diffuses into the gaseous medium, then it leads to higher burning rate and HRR. However, this last statement implies that a part of the oxygen involved in the reaction would not be considered in the calculations and could lead to underestimate the HRR when oxygen consumption principle is used. Indeed, the two calori-

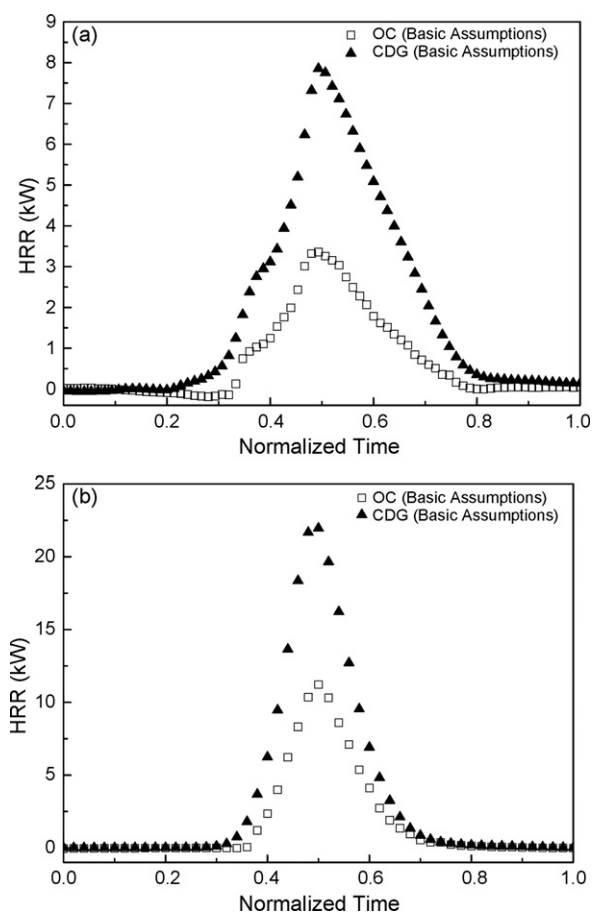


Fig. 6. Comparison of calculated heat release rates by mean of oxygen consumption and carbon dioxide generation basic equations and assumptions. (a) 40% KNO_3 powder, (b) 50% KNO_3 powder, incoming flow rate: 200 l/min.

Table 3

Relative peak deviation between the HRR estimation obtained from oxygen consumption calorimetry and carbon dioxide generation calorimetry.

Smoke powder	Relative standard deviation of peak values	Relative standard deviation of total energy values
40% KNO_3	53%	56%
50% KNO_3	44%	46%

metric methods show different results. All calculations emphasize that the rate calculated through OC is lower than the one obtained by CDG. Table 3 shows the relative deviation for the peak values of HRR estimations and for the total energy from the two methods. The evaluation of HRR by CDG is about twice as high as that calculated by OC Calorimetry.

Several comments can be made on the results. Firstly, the deviation between the two methods slightly decreases with a higher oxidizer concentration (cf. Table 3). A comparison of the depletion in oxygen shows that the one obtained for the 50% KNO_3 powders is roughly seven times higher than the one found for the 40% KNO_3 powder. Nevertheless, the amount of fuel and the experimental conditions are the same in every case; only the concentration in oxidizer changes. Given the homogeneity of the mixture, when the KNO_3 decomposition starts by means of a pilot energy (endothermic reaction), oxygen is released directly in the vicinity of the fuels so the combustion can occur. One hypothesis is to assume that the pilot energy starts decomposing the fuels into volatiles as well as KNO_3 into K_2O , N_2 and O_2 . When ignition occurs, O_2 released by KNO_3 is already diffusing through the gaseous medium and will then participate in the combustion as the main reaction partner. The heat released provides energy to sustain the oxidizer decomposition. In a second time, the oxygen from the air combines with the O_2 supplied by KNO_3 to feed the combustion process [8]. By increasing the concentration of oxidizer in the mixture, the O_2 diffusion through the gaseous medium becomes more important. The amount of volatiles is in contact with more O_2 which leads to an increase of the burning rate and a decrease of the combustion time.

On the other hand, it appears clearly that the O_2 concentration could be an issue for using the species evolution approaches to calculate the HRR. The amount of O_2 consumed during the combustion cannot be evaluated with a standard method based on an analyser measurement. By neglecting the internal amount of O_2 released from the KNO_3 decomposition, the calculated oxygen consumption would be underestimated in regard to the actual one. Finally, the HRR would as well be underestimated compared to the carbon dioxide generation as it emerges in the Fig. 6.

The prediction of the heat release rate is influenced by the oxygen concentration. Nevertheless, the HRR calculation by calorimetry is based on several assumptions that could likely be no longer valid for energetic materials. As an example, the heats of combustion used in both methods are assumed. These values have been estimated for standard fuels but questions remain regarding complex materials like smoke powders. On the other hand, it is also imperative to check the sensitivity of the HRR calculation with regards to the mass flow rate of the exhaust gases, the water vapour molar fraction and the exhaust gases molecular weight. These last factors appear in both calorimetry methods but it is necessary to know their influence on the calculation. The validity of the assumptions has been investigated in different studies by estimating the uncertainty on HRR obtained from calorimetric calculations [24–26]. A sensitivity analysis has also been carried out in a previous work [27]. Results are summarized in Table 4. The two main factors able to influence HRR calculation in case of energetic materials are the oxygen concentration and the energy constants. The exhaust flow rate can also significantly alter the HRR, particularly

Table 4
Heat release rate sensitivity analysis.

Variable	Nominal value	Variation frame	Peak HRR sensitivity	Total energy sensitivity
E_{O_2}	13.1 kJ g ⁻¹ of O ₂	[5–25 kJ g ⁻¹ of O ₂]	0.75 kW/(kJ g ⁻¹ of O ₂)	13.24 kJ/(kJ g ⁻¹ of O ₂)
E_{CO_2}	13.3 kJ g ⁻¹ of CO ₂	[5–25 kJ g ⁻¹ of CO ₂]	1.45 kW/(kJ g ⁻¹ of CO ₂)	23.6 kJ/(kJ g ⁻¹ of CO ₂)
$X_{O_2}^A$		[19–21%]	0.93 kW/(0.1% of O ₂)	16.9 kJ/(0.1% of O ₂)
$X_{H_2O}^A$		[0–5%]	0.06 kW/(% of H ₂ O)	0.89 kJ/(% of H ₂ O)
\dot{V}_e	160 N m ³ /h	[100–235 N m ³ /h]	0.07 kW/(N m ³ /h)	5.13 kJ/(N m ³ /h)
α	1.105	[1–2]	0.05 kW/(0.1 of α)	0.67 kJ/(0.1 of α)

if the Pitot tube coefficient has not been specially calibrated for the apparatus.

Regarding the OC calorimetry method, oxygen molar fraction is the most sensitive variable [27] but the energy constant can also induce large variations in the results. In the case of CDG calorimetry, the sensitivity to the O₂ molar fraction remains relatively low. However, the energy constants are a critical parameter that needs to be evaluated with care.

The peculiarity of energetic materials poses a problem in evaluating correctly the amount of oxygen consumed by the combustion reaction through the analyser. It is essential to identify the source(s) of the discrepancies between the two calorimetry methods.

5. Correction procedure

5.1. OC/CDG divergence

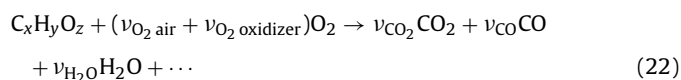
Fig. 6 shows important divergence between HRR calculated through OC and CDG. A sensitivity analysis allowed highlighting the few parameters likely to significantly modify the calculation results: the exhaust flow rate, the O₂ molar fraction and the energy constants. In order to analyse the divergence of the OC and CDG methods, their ratio is calculated;

$$r_{CDG/OC} = \frac{E_{CO_2}(\dot{m}_{CO_2} - \dot{m}_{CO_2}^o) + E'_{CO} \dot{m}_{CO}}{E_{O_2}(\dot{m}_{O_2}^o - \dot{m}_{O_2})} \quad (21)$$

Every mass rate in Eq. (21) is function of the exhaust flow rate \dot{V}_e . $r_{CDG/OC}$ presents the advantage to be independent of \dot{V}_e . Thus, the influence of the exhaust flow rate can be investigated. Ratio of CDG to OC calorimetry has been calculated for a set of tests realised with heptane fuel. Total energy and HRR peaks have been considered. As expected, ratio obtained was very close to 1. The same ratio has been calculated for smoke powders. Results for the total energies and the peaks tend to spread around a mean value of 2.15 ± 0.30 (cf. Fig. 7). Discrepancy is present. Given the independency of $r_{CDG/OC}$ to the exhaust flow rate, the most likely parameters to interfere in the heat release rate calculation are the oxygen molar fraction and the energy constants.

5.2. Corrective method

The hypothesis is that the divergence between the two methods raises from the neglected amount of O₂ produced by the KNO₃ decomposition and consumed during the combustion while only O₂ from air was considered in the calculation. The chemical reaction to be considered is given by,



Being able to evaluate the rate of O₂ supplied by the decomposition of KNO₃ to the fuel mixture (starch/lactose) would allow to use the calorimetric equations with general assumptions.

Freeman [22] has ascertained the thermal decomposition of KNO₃ (cf. Eqs. (23) and (24)).



2nd decomposition reaction ($T > 750^\circ\text{C}$):



From a mass balance of the residues, it emerges that the thermal decomposition of KNO₃ reached the second stage. However because of the complexity of the mixture, it has not been possible yet to define the kinetic of the reactions. Additional thermal analysis would be necessary (Differential scanning calorimetry, Thermogravimetric analysis, Differential thermal analysis, Mass spectrometry) to build a decomposition model of the mixture. The assumption of a homogeneous burning (i.e. for the 50% KNO₃ powder, $\dot{m}_{\text{starch}} = \dot{m}_{\text{lactose}} = 0.5\dot{m}_{KNO_3}$ with all KNO₃ decomposing into K₂O would not be valid here. KNO₃ starts decomposing before volatiles are being produced. Moreover, the composition of starch and lactose shows a large number of C–O bonds, which makes the use of E_{O_2} and E_{CO_2} not relevant (The energy related to C–O bonds is relatively different to the C–H energy bond). Finally, estimating the rate of O₂ supplied by the oxidizer appears relatively complex.

However, it has been previously demonstrated that energy constants can significantly alter the HRR [27]. Huggett's and Tewarson's constants have been defined for standard fuels [19,17]. Their validity for compounds such as energetic materials has to be established. Actual energy constants can be estimated if the heat of combustion of the material is known as well as its composition in order to balance the stoichiometric combustion equation. Correct estimation of HRR can be achieved by defining energy constants adapted to the tested powders.

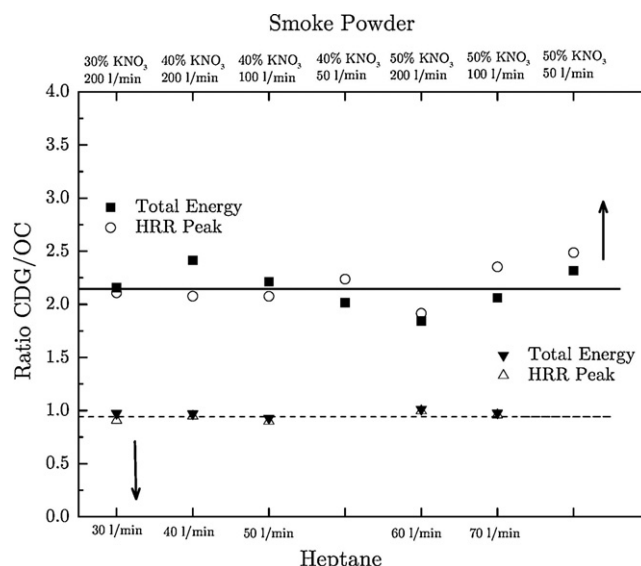


Fig. 7. Ratio of HRR results obtained by CDG to HRR results obtained by OC.

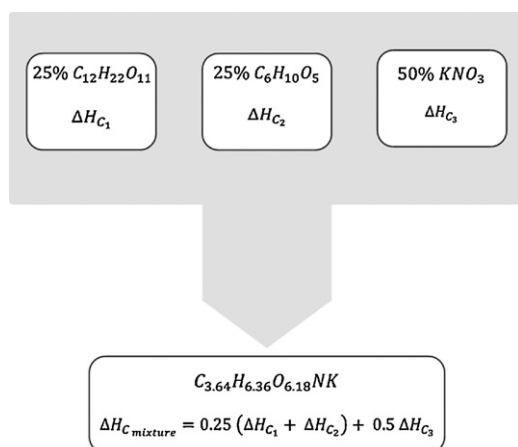


Fig. 8. Fictitious molecule and heat of combustion related.

Table 5

Heats of reaction of the compounds present in the 50% KNO_3 material and heat of combustion of the fictitious molecule.

Material	$\Delta H_{\text{reaction}}$ (kJ g^{-1})
Starch ($\text{C}_6\text{H}_{10}\text{O}_5$)	-17.5 (Combustion)
Lactose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$)	-16.5 (Combustion)
$\text{KNO}_3 \rightarrow \text{K}_2\text{O}$	6.21 (Thermal decomposition)
Fictitious molecule $\text{C}_{3.64}\text{H}_{6.36}\text{O}_{6.18}\text{NK}$ ($M = 202 \text{ g mol}^{-1}$)	-5.4 (Combustion)

The heat of combustion of the two tested powders is unknown. However, by knowing their composition and assuming the decomposition of the oxidizer (Eqs. (23) and (24)), estimations can be obtained. The heats of combustion of lactose and starch are known as well as the energy required to decompose KNO_3 . Taking into account the mass balance and the assumed decomposition of the oxidizer, a fictitious molecule can be modelled, encompassing the fuel components and the O_2 generated by KNO_3 (cf. Fig. 8). By energy balance, the heat of combustion of the fictitious molecule can be calculated (cf. Table 5). The new energy constants can be calculated using Eqs. (6) and (8). The advantage of the technique is that it considers the decomposition of the oxidizer and does not require a correction to account for the internal amount of O_2 . HRR results are presented on Fig. 9. The relative standard deviation between the two calorimetric methods is less than 10%.

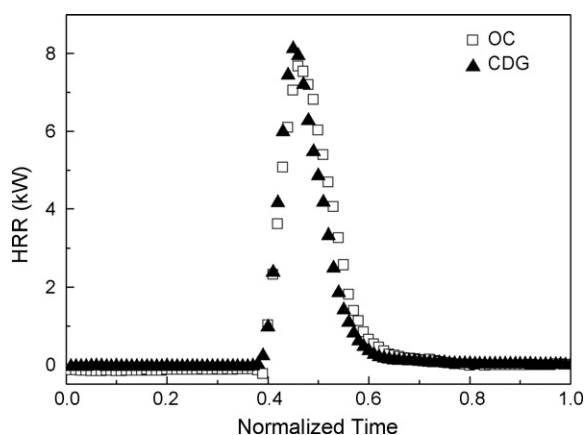


Fig. 9. HRR comparison from OC and CDG estimations with calculated energy constants for a 50% KNO_3 material.

Finally, a convergence of HRR estimations by means of OC and CDG principles from the tested energetic material has been achieved. A method based on estimating the energy constants from the material chemistry seems to lead to a consistent result. It shows that to predict the HRR for materials such as smoke powders, a chemical decomposition model, as well as the heat of combustion and the chemical composition of the mixture are necessary. However, to conclude on the degree of accuracy of the HRR results will require to estimate the heats of combustion of the tested materials and to verify the validity of the fictitious molecule assumption.

In the future, bomb calorimeter analysis will be carried out on the tested powders in order to define their heats of combustion. HRR estimations obtained by means of OC and CDG can then be compared to HRR evaluated through mass loss data.

6. Conclusions

Calorimetry laws were developed in the 1980s and have become widely used for HRR calculations. They have been validated for a large number of materials thus there is an increasing feeling that they can be used for all materials with no limitations. The purpose of this study was to investigate the suitability of OC and CDG principles to achieve accurate HRR estimations when burning smoke powders using the Fire Propagation Apparatus (FPA).

Reactions involving these types of materials are relatively fast but it was shown that the FPA is able to provide consistent data to allow the evaluation of the HRR. Using general assumptions, results show discrepancies between the standard analysis techniques. CDG calorimetry gives an estimation of the HRR higher than the one obtained by OC calorimetry. A previous sensitivity analysis emphasized that the level of completeness of the oxygen concentration and energy constants calculation significantly affected the HRR estimation. This has not been apparent for most fire related materials.

The consumption of oxygen measured by the analyser underestimates the actual consumption because of the presence of the oxidizer in the mixture. A viable and necessary correction is to estimate the internal supply.

A correction for the energy constants has also been shown to be necessary and the oxygen supply correction was not found sufficient, in the studied cases, to obtain an accurate estimation of the HRR. Energy constants taking into account the decomposition of the oxidizer have been calculated and their use lead to converging results for OC and CDG. This correction method has therefore been proven viable with the inherent limitation that this technique requires knowledge of the burning material as well as of its chemistry. Further verification of this approach is currently in progress by means of mass loss and bomb calorimetry measurements. The chemistry associated with the decomposition of the material will be assessed via Fourier Transform Infrared Spectrometer (FTIR), Differential Scanning Calorimetry (DSC) and Thermogravimetric (TGA, DTA) analyses.

The need for a prior knowledge of chemistry and composition reduces somewhat the value of this type of testing, but remains essential to derive toxicity data on the effluents. The way to go forward likely relies in the development of generic constants that apply to sub-categories of energetic materials to keep a practical means to obtain the HRR with reasonable accuracy.

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