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Accuracy (trueness and precision) of cone calorimeter tests with and without a vitiated air enclosure

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Abstract

Over the last few years, new many laboratory fire tests have been developed. One such test is the controlled atmosphere cone calorimeter (CACC). Until now this bench-scale test has not been standardized and the device design differs from one laboratory to another. These differences can affect measurement accuracy^b (trueness^c and precision^d) and direct comparison of literature results is difficult. No studies have been conducted to understand the effect of the design on the fire behaviour of materials and measurement accuracy in the CACC. The present publication focuses on these effects under ambient and non-ambient oxygen conditions. Several designs were investigated using Poly(methyl) methacrylate (PMMA) as the test material. Statistical analyses were performed in some cases to assess the data. The results are presented and discussed.

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1. Introduction

The flammability of materials is of intense interest in fire safety research. Unlike combustible gases or liquids, where the word “flammable” has a precise definition and whose fire properties can be quantified in terms of flammability limits and flashpoint, there is no single parameter to quantify the potential fire risk of a combustible solid. The so-called “fire properties” of combustible solids are commonly listed as ease of ignition, rate of surface spread of flame, rate of heat release and propensity to produce smoke and toxic gases. However, these parameters cannot be defined as “true” material properties such as thermal transport properties for instance. Indeed, they depend on the size configuration, the orientation of the sample and on environmental conditions. The reaction-to-fire of combustible materials can depend on physical factors related to the tested product as well as its environment and/or chemistry. For this reason, when the term “flammability” is applied to solids, it must relate to the total system in which the nature, the physical form, the orientation of the materials, and the fire environment are defined.

Over the last few years, new laboratory fire tests have been developed to study the flammability of products [1]. These standard test methods are used to rank materials according to their fire performance. During these tests, the physical form and orientation of products are specified and the fire environment is strictly controlled. The rank order of combustible materials can change significantly if these specifications are altered. As a consequence, the tests whose purpose is to

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^b Accuracy: The closeness of agreement between a test result and the accepted reference value.

^c Trueness: The closeness of agreement between the average value obtained from a large series of test results and an accepted reference value.

^d Precision: The closeness of agreement between independent test results obtained under stipulated conditions.

measure the same property can place a set of selected materials in widely differing rank order. This apparatus dependency is a serious problem [2].

One of the most important bench-scale instruments for fire testing is the *cone calorimeter*, which was developed in the early 1980's. The standard cone calorimeter has been adopted in research laboratories as a reference tool to measure the characteristics needed to assess the fire hazard of a material. The basic apparatus is described in a series of publications [3, 4] and was defined in detail in the international standard ISO 5660-1 [5]. The cone calorimeter derives its name from its radiant heat source, shaped as a truncated cone. These tests were performed to evaluate not only pyrolysis and combustion conditions, but also the fire behaviour of a small sample ($\sim 0.01 \text{ m}^2$) burning under well-ventilated conditions. The sample size is of the smallest order of magnitude discussed in fire engineering and of the largest used in polymer analysis. Nevertheless, this apparatus constitutes an important link between fire engineering and polymer science, which is crucial in the interdisciplinary area of fire science. Indeed, it provides comprehensive insight into several flammability characteristics, such as the heat release rate, the total heat release, and the time to ignition [3, 4]. It has been also used to measure the smoke and gas production [6-8]. The cone calorimeter design was developed thoroughly to target the properties of materials [5] rather than to correspond to a special full-scale scenario of a real fire. Cone calorimeter investigations are usually used as a universal approach to rank and compare the fire behaviour of materials. Therefore, it is not surprising that the cone calorimeter is finding increasing implementation as a characterization tool in the research and development of fire-retarded polymeric materials for instance. Nevertheless, it is difficult to reproduce with cone calorimeter a large variety of fire stages [9,10], as its open design even considers an approximately 21vol% oxygen concentration of the incoming air. During a real fire, parameters such as the heat release rate, the smoke production rate, etc. might be affected by both the rate of ventilation and the oxygen concentration [11]. One of the main criticisms of the standard cone calorimeter design is that its use is limited because it is well ventilated. It is a general-purpose tool capable of representing only various fire conditions under ambient oxygen conditions. Measured values such as heat release rate, mass loss rate or CO_2 yield are properly measured with the standard Cone Calorimeter, in well-ventilated conditions. In contrast, measurements such as the CO yield and smoke yield are not properly estimated and limited to well-ventilated conditions. Therefore, the standard Cone Calorimeter cannot be used for toxic potency assessment of polymer material.

To extend test conditions, research instruments capable of evaluating the reaction-to-fire of materials under non-ambient oxygen conditions have been developed. One such instrument is the *controlled atmosphere cone calorimeter* (CACC) also designed in literature as the *modified cone calorimeter*, *vitiated cone calorimeter*, or *controlled ventilation cone calorimeter*. The device was introduced by references [12-15] and then adopted by numerous authors [16-33] and also mentioned by Hull [34], Babrauskas [35], and Mouritz and Gisbon [36]. This apparatus is designed by attaching an enclosed vitiated air chamber (VAC) to the standard Cone Calorimeter. The fire conditions of this chamber may be controlled such as the oxygen content for instance. Despite the design, the fire parameters, which can be measured in the CACC, are the same as the ones in the standard cone calorimeter such as the heat release rate, the smoke rate, etc. From the development of the CACC to its utilization, a small number of research projects have been conducted over the last twenty years investigating the use of the controlled atmosphere cone Calorimeter compared to the standard cone calorimeter. Table 1 gives the state of art of twenty years of research with a controlled atmosphere cone calorimeter. These works report mainly the effects of mass flow rate in the exhaust duct, oxygen content or irradiance level on the heat release rate or the gases yield. This device has also been used to study the effect of an oxygen-enriched environment on the fire behavior of polymer materials [14, 16-33].

Due to the lack of international standards on this test apparatus, it is important to note that the CACC design and volume of the VAC may fully change from one testing laboratory to another. In some works, it is placed below the standard exhaust hood with a direct connection to the hood, as shown in Table 1. In more common cases, there are no direct connections between the VAC and the exhaust hood. In fact, the VAC can be sold separately and this device can then be installed below the exhaust hood of the standard cone calorimeter. For this reason, the majority of works have no direct connection. A chimney was sometimes used on the top of the cone heater to prevent backflow of ambient air and to avoid effluent burning in ambient air as it emerges from the combustion chamber ultimately giving well-ventilated flames. This design was proposed by Hietaniemi et al. [22, 23] and adopted by MARQUIS and Guillaume [29-31] and Werrel et al. [32, 33]. So far, authors do not use the same dimensions of the chimney. Thereby, the chimney height may vary between 20 and 60 cm. The dependency of the chimney dimensions has not been studied yet. Hietaniemi et al. [22, 23] argues furthermore, that an instantaneous effective global ratio should be used rather than a local equivalence ratio, based on the oxygen supply to the VAC because of the post oxidation of effluent when emerging from the VAC. Indeed, this author specifies that '*in this case the amount available to combustion exceeds the amount that was fed to the combustion chamber*'.

Due to the space between the VAC and the exhaust hood, the exhaust gases are diluted by excess air drawn from the laboratory surroundings. The post-oxidation of gas species that emerge from the VAC and heat-induced changes in the dilution ratio affect the measurement of the oxygen content and the calculation of the heat release rate. Recently, Werrel et al. [32, 33] have thereby showed that the usual formula definition used to calculate the heat release rate was not adapted to

Table 1. State of the art of twenty years of research with a controlled atmosphere cone calorimeter

	Authors	Aims	Materials gas or fluids studied	Design ^a	Experimental Conditions ^b
1991	Mulholland et al. [12]	- Effect of oxygen on fire behaviour - Assessment of CO and CO ₂	Methane, propane, ABS, Polyethylene surlyn, PE with fibreglass and carbon black additive, PMMA with carbon additive, Douglas fir	DC.	Oxygen content: 13.8, 15.1, 17.1 & 21 vol% Irradiance: 15, 25, 30, 40 & 50 kW.m ⁻²
1992	Babrauskas et al. [13]	- Development of CACC		DC	
1992	Petrella et al. [15]	- Effect of oxygen on fire behaviour - Assessment of CO and CO ₂	PMMA	DC	Oxygen content: 15.3, 18 & 21 vol%
1995	Christies et al. [16]	- Effect of oxygen and ventilation rate on fire behaviour - Assessment of CO and CO ₂	PMMA, PIR rigid foam and HCFC-141b	DC	Oxygen content: 15, 18 & 21 vol% Ventilation rate: 9, 15 & 24 L.s ⁻¹
1993-2002	Hshieh et al. [14,17-21]	- Effect of oxygen and irradiance on fire behaviour and gas production - Assessment of CO and CO ₂	Flame retardant cotton fabric [17]; Epoxy and brominated epoxy composite [18]; Silicon fluid and Silicon elastomers [19]; Flame retarded epoxy composite, phenolic composite with fibreglass, aramid, graphite fibre reinforcement [20]; High molecular weight hydrocarbon fluid, 50cS silicon fluid [21]	DC	Oxygen content: 15, 21, 30 & 50 vol% Irradiance: 20, 35, and 50 kW.m ⁻²
1997-99	Hietaniemi et al. [22,23]	- Effect of oxygen on fire behaviour - Assessment of toxic gases with FTIR analyser and chromatography/mass spectroscopy analysis		WC + Chimney	
2000	Dowling and Leonard [24,25]	- Development of CACC - Effect of oxygen and irradiance on fire behaviour - Assessment of CO and CO ₂	PMMA, Wool carpet	DC	Oxygen content: 15, 18 & 21 vol% Irradiance: 20, 35, and 50 kW.m ⁻²
2005	Griffin et al. [26]	- Effect of oxygen on fire behaviour	Fire retardant coating	NS	
2010-11	Gomes et al. [27,28]	- Effect of oxygen on fire behaviour - Assessment of toxic gases with FTIR analyser	PVC	WC	Oxygen content: 18, 21 vol%
2010-11	Marquis and Guillaume [29-31]	- Effect of oxygen and irradiance on fire behaviour and gas production - Assessment of toxic gases with FTIR analyser - Experience plan	Sandwich composite material	WC + Chimney	Oxygen content : 0, 5, 10, 15 & 21 vol% Irradiance: 20, 35, and 50 kW.m ⁻²
2011	Werrel et al. [32,33]	- Development of HRR calculation - Effect of oxygen on fire behaviour	PMMA, Chipboard	WC + Chimney	Oxygen content: 15, 17, 18, 19 & 21 vol%

^a Design of CACC can change from one laboratory to another. This column explains the CACC design used by the author. DC: direct connection between chamber and exhaust hood, WC Without connection between chamber and exhaust hood, NS: Not specified;

^b Variables that changes in the experimental conditions

PIR: Polyisocyanurate, PMMA; poly(methyl)methacrylate, PVC: polyvinyl chloride; ABS: acrylonitrile-butadiene-styrene, PE: Polyethylene surlyn blend;

the CACC design due to this space. Following Janssens's approach [37, 38], Werrel et al. [33] modified these equations to the CACC design. Taking into account the dilution ratio, he published a set of equations that considers incomplete combustion by the generation of carbon monoxide according to Hess' Law.

Hence, no studies have been performed to understand the effects of design on the experimental results. Studies did not verify whether tests performed on presumably similar apparatuses, such as the standard CC and CACC, with identical experimental conditions, provided identical results. We can ask whether using a VAC or changing the test design may affect

the measurement accuracy of the heat release rate or the mass loss rate for instance. Many factors may contribute to the variability of experimental results, such as the operator, the equipment used, the calibration of the equipment, the environment and the time elapsed between measurements. It is useful to remember that the variability of the result can also be attributed to the inherent variation in the measurement procedure. In the practical interpretation of measurement data, this variability must be considered. Although, standardization of the controlled atmosphere cone calorimeter is currently under preliminary discussion within the international committee ISO TC92/SC1/WG5 and ISO TC92/SC3/WG1, the lack of international harmonization does not allow a clear and direct comparison of results with the literature.

The motivation of the present study comes from our interest to study the VAC influence on measurement accuracy^e. In the first part, the present paper introduces the Werrel's approach and the test protocol to calculate the heat release rate taking into account dilution effects. In the second part, the effects of the CACC design were analyzed on a plastic material, s Poly(methyl) methacrylate (PMMA). As a reference fuel material, solid acrylic PMMA polymer has been widely employed – with or without filler – during previous studies to assess the polymer flammability during the combustion process [39-48]. In the present work, the experimental analyses were performed under ambient and non-ambient oxygen conditions. Investigations were carried out following the same test protocol to check the repeatability and reproducibility between test results. The accuracy and precision of the test beds were assessed by means of a statistical analysis in accordance with standard ISO 5725 [49, 50].

2. Experimental setup

2.1. Tested material

The material used in this study is a black non-charring poly(methyl) methacrylate (PMMA), commonly known as Altuglas, supplied by the company VACOUR and synthesized via radical polymerization. Elementary analysis was conducted by a combination of catharometry and ND-IR detection. The elementary analysis results show that no inert load, flame-retardants or fillers were used during the manufacturing of the PMMA sample; neither chlorine nor sulphur-based additives were found. Indeed, 100 wt% of the total sample mass is composed of C, H and O atoms. Based on this elementary analysis composition, the raw chemical formula of the virgin PMMA was determined to be $(C_{4.9}H_{7.8}O_{2.0})_n$ (with n = PMMA polymerization degree).

Specimens were conditioned at (23 ± 2) °C and at a relative humidity of (50 ± 5) % for more than 88 hours in accordance with the specifications of the ISO 291 standard [51]. The sample dimensions were (100 ± 2) mm long, (100 ± 2) mm wide and (14 ± 1) mm high, with a mass of (170 ± 10) g. The mass densities measured by pycnometer method [52], are equal to (1214 ± 61) kg.m⁻³.

2.2. Standard cone calorimeter ISO 5660-1

The cone calorimeter is one of the basic fire tests, developed by Babrauskas in the eighties [3, 4]. The bench-scale test is now an international standard ISO 5660-1 [5] and is beginning to be widely used in some regulations, especially in transportation applications. The reader can find a complete description of the test apparatus in this standard.

2.3. Controlled atmosphere cone calorimeter

Small-scale experiments were carried out with a controlled-atmosphere-cone-calorimeter (CACC) at the LNE. The experiment is described in detail elsewhere [12-15] and only a brief description is presented here. This test apparatus (Fig. 1) has been developed to study the influence of depleted oxygen environments on thermal degradation and combustion. The main difference with the standard test unit is that an enclosure has been added under the cone heater. This enclosure box is placed below the standard exhaust hood without a direct connection. The specimen under test and the load cell are situated in the VAC. This chamber consists of a stainless steel enclosure, with the standard cone heater on the top, a door with an observation window on the front and two gas inlet ports at the bottom. Through the gas ports, the attachment is supplied with a mixture of air and nitrogen to create the desired ambient atmosphere and to adjust the desired oxygen and nitrogen concentrations. The mixture is maintained at a suitably low flow rate through the enclosed vitiated air chamber to facilitate the recirculation of combustion products over the specimen surface. The atmosphere is adjusted by one rotameter

^e The understanding of the meaning of these basic terms (*i.e.* precision, trueness and accuracy, repeatability and reproducibility) use to describe the quality of a measurement has sometimes proven difficult. For detailed information, we refer the reader to the standard ISO 5725 [49, 50] to understand all the definition and differences between the terms used here.

respectively for the volume flow of air and nitrogen. Mixing is monitored by an additional oxygen analyzer, which is directly connected to the VAC. To limit radiation from the enclosure, a cooling rig is placed between furnace and topside of the box. The oxygen concentration in the enclosure can be adjusted to any value from 21 vol% down to 0 vol%. It can also be used with oxygen concentration higher than 21 vol%.

The test method uses a test specimen of the same size as the cone calorimeter with a surface area of $100 \times 100 \text{ mm}^2$. A truncated shaped-cone heater exposed the specimen to a constant irradiance level (up to 100 kWm^{-2}). A spark plug above the test specimen ignites any flammable gases. The effluents are then collected in a hood and transported through a duct equipped with a thermocouple, a pressure sensor, a smoke measurement system and a sample probe for O_2 , CO and CO_2 analyzers.

The fire parameters, which can be measured in the CACC, are the same as the standard cone calorimeter: heat release rate, mass loss rate, smoke density, gas compounds, etc. This device also allows quantification of the production rate of chemical species, which depends on the oxygen concentration.

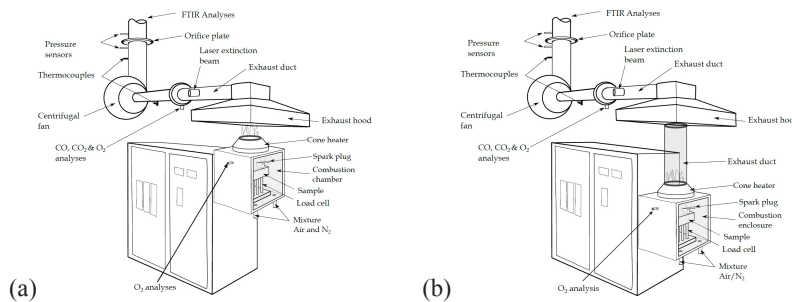


Fig. 1. (a) Controlled-atmosphere cone calorimeter apparatus (b) Controlled-atmosphere cone calorimeter apparatus with quartz exhaust duct above the enclosure-box attachment to reduce the effluent post-oxidation.

However, the use of CACC without connection has some limitations. It is difficult for a controlled-atmosphere cone calorimeter to provide relevant data for low oxygen concentrations because of the possible oxidation of smoke between the VAC and downstream exhaust sampling point for heat release rate and FTIR species measurements. In some cases ($X_{\text{O}_2} > 10 \text{ vol\%}$) [22, 23], the effluent may continue to oxidize as it emerges from the chamber ultimately giving well-ventilated flaming. To reduce the oxidation phenomenon and burning of gaseous products outside the test chamber, a 60 cm quartz or metallic exhaust duct was mounted on the top of the cone heater, as shown in Fig 1.b. This chimney prevents backflow from ambient air and avoids flames occurring in the ambient air. Using a quartz chimney allows observation of flames in the upper flow and ensures that gases cool when mixed with air in the exhaust hood, leading to a reduction in the post-oxidation phenomenon. It is possible to use the ISO 13927 metallic exhaust duct [53], which is equipped with a thermopile detector. This thermopile could be used to estimate the heat release instead of the more accurate oxygen consumption techniques. In the present paper, this technique is not used to measure the heat release.

2.4. Equivalence ratio

One parameter commonly used to describe ventilation conditions during combustion is the equivalence ratio. This concept has its origin in combustion studies of well-mixed fuel-oxidizer mixtures. It is defined as follows [54-56]:

$$\phi = \frac{\dot{m}_F / \dot{m}_{\text{Ox}}}{(\dot{m}_F / \dot{m}_{\text{Ox}})_{st}} = r_{\text{Ox},st} (\dot{m}_F / \dot{m}_{\text{Ox}}) \quad (1)$$

where \dot{m}_F is the mass loss rate of fuel, \dot{m}_{Ox} is the oxidant mass flow rate, $r_{\text{Ox},st}$ is the ratio of oxygen and fuel mass rates at stoichiometric conditions, and the subscript *st* refers to the quotient under stoichiometric conditions. The parameter ϕ describes the relationship between the fuel/oxygen ratio prevailing during fire and the stoichiometric fuel/oxygen ratio. The relationship between the equivalence ratio and the product yield has been studied in detail for a wide range of materials [23, 56-58].

In the context of fires with substantial differences in local fuel and oxidizer concentrations, such as in CACC testing, Eq. (1) is ambiguous. Hietaniemi et al. [23] claim that an instantaneous effective global equivalence ratio ϕ_{eff} should be

used, rather than an average local equivalence ratio, based on the oxygen supply to the chamber, because the combustible products outside the test chamber can burn: “...in these cases, the amount of oxygen available for combustion exceeds the amounts that were fed to the test chamber”. The author defines the effective global equivalence ratio characterizing the global oxygen availability to the system as:

$$\varphi_{eff} = r_{Ox_{st}} (\overline{\dot{m}}_F / \dot{m}_{Ox,eff}) \tag{2}$$

where $\overline{\dot{m}}_F$ is the time averaged fuel mass loss rate and $\dot{m}_{Ox,eff}$ is the effective oxygen mass flow rate. Eq (2) proposed by Hietaniemi et al. lead to an equivalence ratio range less than unity whereas Eq. (1) can give values higher than unity.

Up until now, however, the concept could only be used in situations where fuel and airflow could be accurately metered and the chemical composition of the fuel is known. This is not the case for most “real” materials with multi-fuel compositions etc, where the equivalence ratio may change in depth and in time. In this case, it is more appropriate to study the link between the data and the effective oxygen content in the test chamber of the CACC. This philosophy was applied in the present study.

2.5. Experimental procedure

Experiments were performed using four configurations of the cone calorimeter, as shown in Fig. 2: (a) the standard cone calorimeter ISO 5660 [6], (b) the CACC without an exhaust duct, (c) the CACC with a 60 cm quartz exhaust duct, and (d) the CACC with a 60 cm metallic exhaust duct in conformity with ISO 13927 [53].

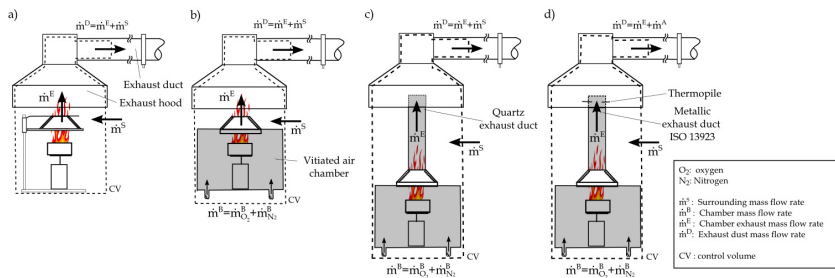


Fig. 2. Schematic views of the four different configurations of cone calorimeters: General representation of the combustion system including volume control used for mass conservation. (a) Standard cone calorimeter ISO 5660-1, (b) Control-atmosphere cone calorimeter, (c) Modified CACC with a 60 cm quartz exhaust duct and (d) Modified CACC with 60 cm metallic exhaust duct ISO 13927.

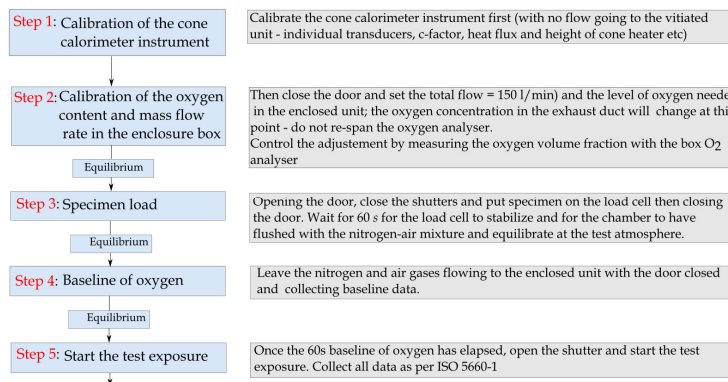


Fig. 3. Adapted test protocol used for the CACC designs to determine the oxygen baseline.

The test procedures were similar to those described in the international standard ISO 5660-1 [5] with one exception: for CACC tests (Fig. 2b-d), the samples were in a vitiated air chamber. All samples were tested in a horizontal position. The data were evaluated using the decreased surface area of the sample (0.008836 m²) Measurements were performed with

insulation on the backside of the sample. The silica wood insulation blanket used had a density of $64 \text{ kg}\cdot\text{m}^{-3}$ as described in the ISO 5660-1 standard [5].

During these experiments, the ventilation rate \dot{v}^D was taken to be equal to $(24 \pm 2) \text{ dm}^3\cdot\text{s}^{-1}$ at 23°C . The measured admission volume flow rate in the VAC \dot{v}^B is equal to $(2.667 \pm 0.083) \text{ dm}^3\cdot\text{s}^{-1}$ [e.g. $(160 \pm 5) \text{ L}\cdot\text{min}^{-1}$] at 23°C . Several radiant fluxes or irradiance of the cone heater were used: 20, 35 and $50 \text{ kW}\cdot\text{m}^{-2}$. Data were collected with a 5 s sampling interval.

For the CC design the test protocol is defined in standard ISO 5660-1 [5]. Nevertheless, this one cannot be used for the CACC designs (Figs. 2b-d) and an adapted test protocol was necessary. The test protocol used in the present study is defined in Fig. 3. It is close to Werrel et al. proposal [32, 33], except an oxygen baseline performed after introduction of the sample.

Comparisons between tests were then performed on six characteristics: the transient heat release rate per unit surface area of fuel ($\dot{q}''(t)$) the mass loss rate per unit surface area, the peak of the heat release rate per unit surface area (\dot{q}''_{max}), the maximum average rate of heat emission (MARHE), the average specific mass loss rate (\bar{m}'') and the effective heat of combustion. In the present paper, the influence of design on the emitted products (gases + particulate) is not presented. These results will be presented in future publications.

2.6. Measurements data

When performing fire testing, the Heat Release Rate (HRR), is one of the most important quantities for the fire hazard material evaluation [59] since it controls the rate of fire growth, including heat and production of gas species. The heat release rate is not directly measured but is inferred from other direct measurements. The most common method to measure HRR is known as “oxygen consumption calorimetry” [37, 60]. It is based on Thornton’s theory [61]. Following his approach, most combustibles (gas, liquid or solid) release a constant amount of energy for each unit mass of oxygen consumed. This constant also known as the “Thornton factor” has been found to be $13.1 \text{ MJ}\cdot\text{kg}^{-1}$ oxygen consumed and is considered to be accurate within $\pm 5\%$ for most hydrocarbon fuels [56, 62]. When the composition and heat of combustion of the material are known, a more accurate value could be calculated based on the theoretical stoichiometric combustion equation. After ignition, all of the combustion products are collected in a hood and removed through an exhaust duct in which the flow rate and composition of the gases is measured to determine how much oxygen has been used for combustion. The HRR can therefore be computed using the constant relationship between the oxygen consumed and the energy released. For the standard cone calorimeter, the calculation of the heat release rate is based on Janssens’ work [37, 38]. He published a set of equations to calculate the HRR based on Huggett’s proportionality of the oxygen consumption. It gives a set of equations that consider incomplete combustion by the generation of carbon monoxide and according to the HESS Law. Nevertheless, the formula proposed by Janssens, and used by the standard CC (following the standard ISO 5660), is not adapted to VAC without direct connection with the exhaust hood. Due to the space between the VAC and the hood, the exhaust gases are diluted by excess air drawn from the laboratory surroundings. The heat-induced changes in the dilution ratio affect the measurement of the oxygen content and the calculation of the heat release rate. Thereby, Werrel et al. [32, 33] showed that the error increases at a significant order of magnitude ($\approx 30\%$) when the oxygen content in the enclosure is decreased below 18 vol %. Following Janssens’s approach [37, 38], Werrel defined another formula [Eq. (3)] to calculate the heat release rate $\dot{q}(t)$ (in kW), correcting the pre-experimental oxygen intake for each time step. Werrel et al. approach [32, 33] is summarized in Eq. (3) to (8)

$$\dot{q}(t) = 1.10 \cdot \Delta h_{O_2} \cdot X_{O_2}^i \cdot \dot{m}^D \cdot \left[\frac{\phi - 0.5 \left(\frac{\Delta h_{CO}}{\Delta h_{O_2}} - 1 \right) \cdot (1 - \phi) \cdot (X_{CO} / X_{O_2})}{(1 - \phi) + \phi(1 + (\beta - 1)X_{O_2}^i)} \right] \cdot (1 - X_{H_2O}^S \cdot \tilde{\gamma}) \quad (3)$$

with the oxygen depletion factor ϕ defined by Eq. (4):

$$\phi(t) = \frac{X_{O_2}^i (1 - X_{CO_2} - X_{CO}) - X_{O_2} (1 - X_{CO_2}^S \tilde{\gamma})}{X_{O_2}^i (1 - X_{O_2} - X_{CO_2} - X_{CO})} \quad (4)$$

where Δh_{O_2} is the net heat of combustion per unit mass of oxygen consumed (also known as the Thornton factor and assumed to be $12.98 \text{ MJ.kg}^{-1} \pm 5 \%$ for PMMA); Δh_{CO} is the net heat release per unit mass of O_2 consumed for the oxidation of CO into CO_2 ($17.6.1 \text{ MJ.kg}^{-1}$ of O_2); β is the stoichiometric dilution factor ($\beta \approx 1.5$ [60]); \dot{m}^D is the mass flow rate (in kg.s^{-1}) in the exhaust duct and it is calculated from the pressure drop and the gas temperature following reference [5]; $\tilde{\gamma}$ is a thermal expansion factor [see Eq. (8)]; X_{O_2} , X_{CO_2} and X_{CO} , are respectively the measured mole fraction of oxygen, carbon dioxide and carbon monoxide in the exhaust duct; $X_{O_2}^i$ is the time dependent intake mole fraction of oxygen; $X_{CO_2}^S$ the measured mole fraction of carbon dioxide in the diluting surrounding air and $X_{H_2O}^S$ is the mole fraction of water in the diluting surrounding air. It is calculated as proposed in Eq. (5):

$$X_{H_2O}^S(t) = \frac{RH}{100} \cdot \frac{P_s(T_a)}{P_a} \tag{5}$$

with RH the relative humidity (%), $P_s(T_a)$ the saturation pressure of water vapour at T_a (Pa) T_a is the air temperature (K) and P_a the air pressure (Pa). $P_s(T_a)$ could be calculated following the Clausius-Clapeyron relation.

The readjusted measured mole fraction of O_2 in the incoming air during the test is given as (Eq. (6)):

$$X_{O_2}^i(t) = X_{O_2}^0 \gamma - X_{O_2}^S (\gamma - 1) \tag{6}$$

where $X_{O_2}^0$ is the measured mole fraction of O_2 in the incoming air prior to the test, and $X_{O_2}^S$ is the measured mole fraction of O_2 in the diluting surrounding air.

As specified by Werrel et al. [33], the heat-induced changing of the dilution ratio in terms of the ratios of the mass flow rate in the exhaust duct prior to the test $\bar{m}^{D,0}$ (in kg.s^{-1}) to the one during the test \dot{m}^D (in kg.s^{-1}) is given by the thermal expansion factor γ as [Eq. (7)]:

$$\gamma(t) = \bar{m}^{D,0} / \dot{m}^D \tag{7}$$

while the dilution ratio of room air components, which are not contained in the vitiated air of the enclosure is defined by the second thermal changeable factor $\tilde{\gamma}$ (Eq. (8)):

$$\tilde{\gamma}(t) = 1 - \dot{m}^B / \dot{m}^E \tag{8}$$

with \dot{m}^E and \dot{m}^B are respectively the mass flow rate in the exhaust VAC (in kg.s^{-1}) and the admission mass flow in the box (in kg.s^{-1}).

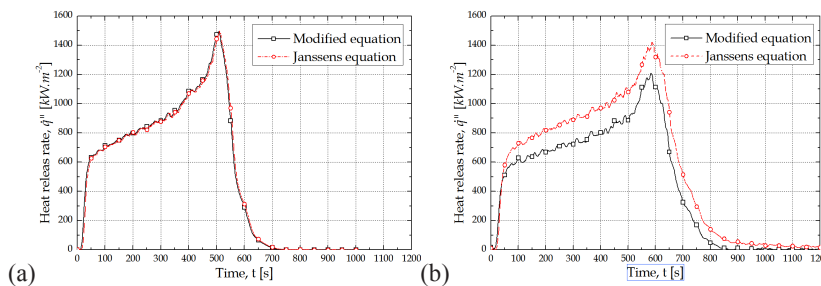


Fig. 4. Calculation of heat release rate both from the conventional equation and from the modified equation (Eq. (3)). Tests were performed on PMMA at 50 kW.m^{-2} with (a) 21 vol% and (b) 15 vol% of oxygen.

Figure 4 presents the application on our material of the heat release rate, using the conventional Janssens equations [37, 38] and modified equations from Werrel et al. [32, 33]. The calculations were performed at 21 vol% and 15 vol% of oxygen.

The results, reported on Fig. 4a, show that Eq. (3) does not affect the heat release rate calculation at 21 vol% of oxygen. While, the heat release rate calculated from the conventional equation achieves higher values than the one calculated by Eq. (3) when the oxygen content is lower than 21 vol%. Hence, the conventional baseline approach does not respect the fact that the oxygen mass flow rate is mainly due to the surrounding air. In that respect, the baseline value, which is assumed to be constant during the test, is therefore overestimated compared to the true value. As highlighted by Werrel et al. [33], this deviation leads to an overestimation of the heat release rate. To correct this error, the adapted baseline approach takes the depletion of the oxygen mass flow rate from the surroundings into account and readjusts the initial baseline value during the test.

The maximum of heat release rate (\dot{q}_{\max}'') occurs when the materials is burning most intensely. It is defined by Eq. (9):

$$\dot{q}_{\max}'' = \max |\dot{q}''(t)| \quad (9)$$

The effective heat of combustion ($\Delta h_{c,eff}$) at time t is characterized as (Eq. (10))

$$\Delta h_{c,eff}(t) = \dot{q}''(t) / \dot{m}''(t) \quad (10)$$

The Maximum average rate of heat emission (MARHE) calculation method determines the average energy value generated during each combustion period in which the HRR value is measured (the integral of the HRR curve during a certain time period represents the energy developed by the specimen during that interval). The points obtained by summing the separate areas and dividing them by the corresponding time gives the ARHE curve (average rate of heat emission), the maximum of which is, by definition, the MARHE (Eq. (11)).

$$MARHE = \max \left| \frac{1}{t_{n+1} - t_n} \int_{t_n}^{t_{n+1}} \bar{q}''(t) dt \right| \quad (11)$$

where $\bar{q}''(t)$ is the mean heat release rate at the time t .

3. Accuracy of the test apparatus

3.1. Influence of test apparatus designs under ambient oxygen conditions

The reaction-to-fire of black non-charring PMMA is governed by the ambient environment (irradiance, oxygen mass fraction, pressure, hygrometry, etc.) and by their chemical and thermophysical properties. A reader can find a complete analysis of the same black PMMA by Luche et al. [48]. The authors deal with a complete and detailed study of thermal decomposition of a black non-charring PMMA in a CC under well-ventilated condition. It includes also the characterization of “apparent” thermal properties and the quantification of exhaust gas concentration.

In the first step, comparisons between test apparatus designs were performed under ambient oxygen conditions *e.g.* with an oxygen content about 20.95 vol%. Fig. 3 reports the average heat release rate and the average specific mass loss rate at three-irradiance levels: 20, 35 and 50 kW.m⁻². The values are averaged over three tests results. Although experimental uncertainties have been evaluated, however they are not presented in order to read more easily the graphs. On these graphs, time $t = 0$ marks the beginning of the exposure to the desired irradiance rather than the ignition delay.

The figure shows the effect of the irradiance level on the ignition delay and the mass loss rate. The ignition of PMMA can be viewed as a series of events [48]. First, the solid must be heated to a high enough temperature for pyrolysis to occur. Once the pyrolysis gases are produced, they mix with the oxidizer to form a combustible mixture. A gas-phase induction process is then initiated by the apparatus’ spark plug. Once the mixture near the igniter has ignited, a pre-mixed flame propagates at the surface of the specimen. In order to initiate sustained burning (equivalent to the fire point), enough pyrolysis gases must be generated at the surface so that the heat release rate of the approaching flame is great enough to overcome so that the heat losses to the solid do not extinguish the flame. The delay to achieve the lean flammability limit is thereby dependent on the irradiance level at the surface of the specimen. Furthermore, Fig. 5 reveals that the intensity of HRR and MLR are amplified with the irradiance level. The amount of energy absorbed by the PMMA and therefore the rate of chemical decomposition (MLR) are strongly dependent on the nature of the spectral emissions of the radiant heat source [2, 62] and the radiative properties of the PMMA. The variation of the heater cone temperature significantly changes

the wavelength range at which the irradiance is distributed. That can modify the rates and depth where the chemical and thermal decomposition occurs.

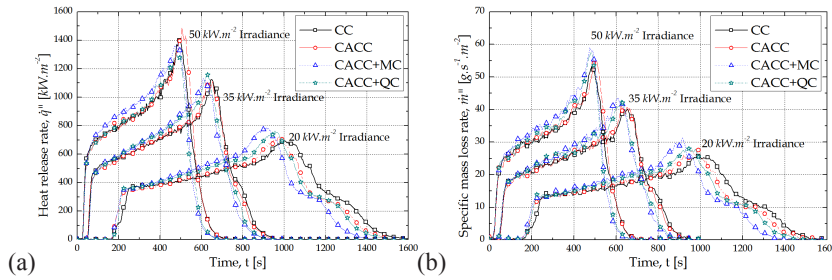


Fig. 5. Comparisons among apparatus for (a) the average heat release rate and (b) the average specific mass loss rate of PMMA at three irradiance levels (20, 35, 50 kW.m⁻²). Measurements were performed under ambient atmosphere.

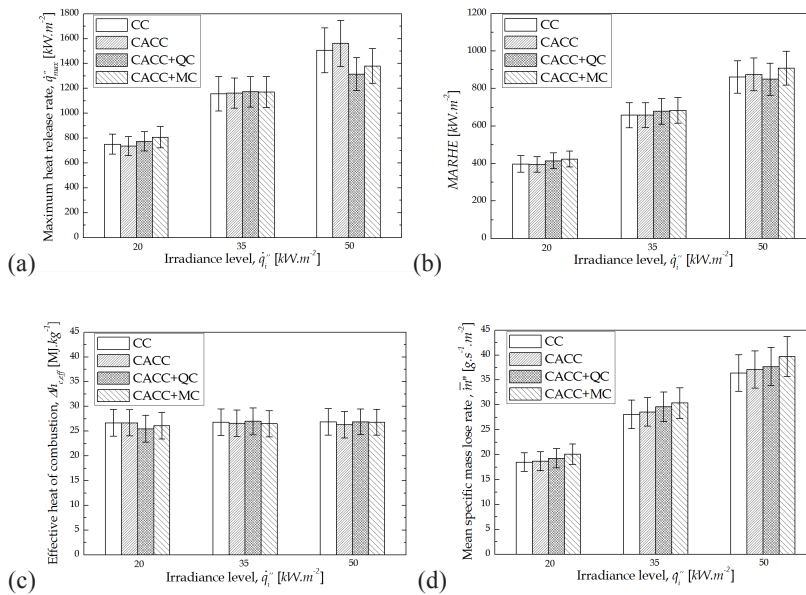


Fig. 6. Influence of design on (a) the maximum heat release rate \dot{q}''_{max} , (b) the MARHE, (c) the effective heat of combustion $\Delta h_{c,eff}$ and (d) the mean specific mass loss rate \bar{m}''_m . The graphs present the average values of three tests and their uncertainties including dispersion and analytical uncertainties. Analyses were performed under ambient atmosphere and for the three irradiance levels tested: 20, 35 and 50 kW.m⁻².

It can be seen that whatever the test apparatus, flaming combustion occurs at the surface of the specimen. In the case of the CACC designs (with and without a chimney), the mass flow in the combustion enclosure and the oxygen content is sufficient to obtain similar conditions to those given by the standard cone calorimeter. Furthermore, the analyses of graphs reveals that the test apparatus designs do not seem to have a significant impact on the decomposition kinetics (specific mass loss rate) and the heat release rate of PMMA at high irradiance. At 50 kW.m⁻², the difference in the results may be due to the speed at which the reactions occurs in the gas and solid phases, given the irradiance level. Thus, we suppose that the high mass flow may lead to cooling of the stainless steel enclosure, reducing its radiation. This trend must however be confirmed by measurement. At 20 kW.m⁻², it can be seen that the small deviation between the values of the SMLR for the various apparatus increases. For the lowest irradiance, the physical reactions, which occur in gas and condensed phase, are much slower. Thus, the deviation between tests apparatus may be related to:

- the effects of the stainless steel enclosure (radiation) on the heating of the PMMA sample;
 - the influence of the chimney on the oxidation of gas species which impacts the thermal decomposition of PMMA.
- Further work is however needed to confirm these trends.

The comparison of tests apparatus cannot be carried out using experimental values without considering measurement uncertainties. For this reason, Fig. 6 gives the values \bar{u}_{ij} average on three test of \dot{q}_{\max}'' , the $\Delta h_{c,eff}$, the $MARHE$, and the \bar{m}'' , with their associated experimental uncertainties. Uncertainties have been estimated following the “Guide to the expression of Uncertainty in Measurement” (GUM) [64]. Uncertainty bars represent both the experimental standard deviation and the measurement uncertainty, with a confidence of 95 %. The reader can find numerous articles on the calculation of uncertainties of the heat release rate in references [65-67].

The deviation observed on the values of the HRR and SMLR (see Fig. 5) is not significant taking into account the uncertainties observed in Fig. 6. No conclusion on observed trends could be confirmed. Therefore, under ambient atmosphere, we show that the design of test apparatus does not have a real impact on the accuracy and repeatability of the measurements.

3.2. Influence of test apparatus designs under non-ambient oxygen conditions

In the second step, the comparisons between the test apparatus design were performed under non-ambient oxygen conditions e.g. in modifying the oxygen concentration in the combustion enclosure. Three designs were compared: the CACC, the CACC + metallic chimney (MC) and the CACC + quartz chimney (QC); the CC test cannot be tested for oxygen concentration different from ambient (21 vol%). Four series of tests were performed to explore the effect of oxygen content on the results. Measurements were carried out at $50 \text{ kW}\cdot\text{m}^{-2}$ and under several contents of oxygen (10, 12.5, 15 and 21 vol%). All tests were repeated three times. The extraction volume flow rate through the exhaust duct was $24 \text{ dm}^3\cdot\text{s}^{-1}$ at $23 \text{ }^\circ\text{C}$. The measured mass flow in the enclosure box was equal to $(2.667 \pm 0.083) \text{ dm}^3\cdot\text{s}^{-1}$ (e.g. $(160 \pm 5) \text{ L}\cdot\text{min}^{-1}$) at $23 \text{ }^\circ\text{C}$.

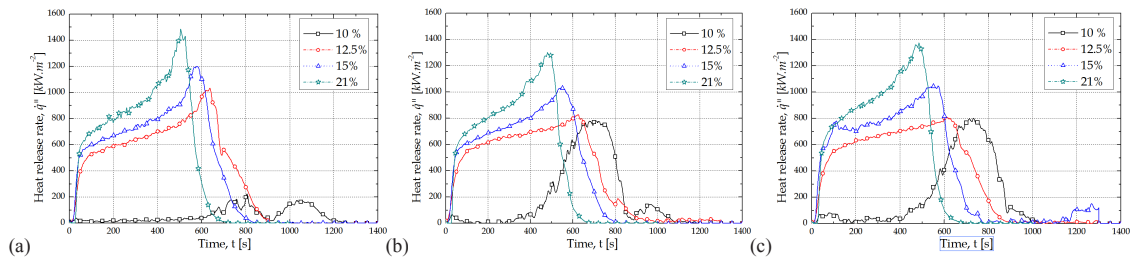


Fig. 7. Comparisons between test apparatus for the heat release rate averaged for three PMMA tests, for several oxygen concentrations (10, 12.5, 15, 21 vol%): (a) CACC (b), CACC+QC and (c) CACC+MC. Measurements were performed at $50 \text{ kW}\cdot\text{m}^{-2}$.

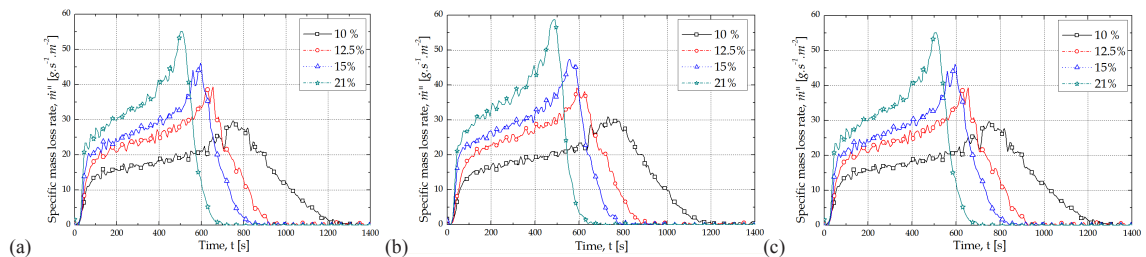


Fig. 8. Comparisons between test on the specific mass loss rate averaged for three PMMA tests, for several oxygen concentrations (10, 12.5, 15, 21 vol%): (a) CACC, (b) CACC + QC and (c) CACC + MC. Measurements were performed at $50 \text{ kW}\cdot\text{m}^{-2}$.

Figures 7 and 8 report the average heat release rate and average specific mass loss rate for all incoming oxygen concentrations tested. The fire behaviour of PMMA strongly depends on the oxygen content. The deviation observed between the kinetics is related to the effects of flame oxidation on the sample surface. The oxidative reactions in the gas phase and radiative feedback of the flame substantially increase the heat flux received by the specimen surface entailing a faster loss of mass. Fig. 7 show that the test apparatus design seems to have a significant impact on the heat release rate of PMMA while Fig. 8 indicates that there was negligible effect on the chemical decomposition rate of the condensed phase. Indeed, the analysis performed on the three designs reveals that the heating up and the chemical decomposition rate of the PMMA sample were identical for a given oxidizer oxygen content. Hence, the design of the test apparatus has no apparent effect on the condensed phase and its chemical decomposition.

On the contrary, the deviation was significant in the gas phase on the heat release rate and gas phase oxidation. From 21 vol% down to 12.5 vol% of oxygen, the gas phase oxidation is more important in the CACC design (See Fig. 7a) than those with a chimney (See Figs. 7b and 7c). In the design without a chimney, the gasified fuel encounters the ambient oxidizer directly when it emerges from the VAC, which favours and amplifies the oxidation of gas species. At these oxygen concentrations, the experimental observations have also shown that the gas dynamics into the VAC allow the oxidization of gaseous species, mainly methyl methacrylate (MMA [68, 69]) but also other species, near the surface specimen. In addition to the shape, the most noticeable difference is the colour appearance of the flame. The air flame is yellow whereas at low oxygen content (12.5 and 10 vol%), as the nitrogen flow is increased, the flame colour tends towards the blue.

At 10 vol% oxygen, this behaviour changes radically. Significant deviations between the heat release kinetics of the three designs can be observed. The heat release rate of the CACC apparatus with the chimney achieved considerably higher than the CACC design with no chimney. This behaviour is counter-intuitive. We could have expected that the oxidation is more important in the CACC design because of post-VAC oxidation reaction. Nevertheless, Fig. 7a shows the contrary at 10 vol% of O_2 . In fact, at this oxygen concentration, the mixture of gas and oxidant is close to its lean flammability limit (LFL). In the case of the CACC + MC and the CACC + QC apparatus, the ignition occurs near the igniter. The flame is diffused in the chimney in the whole fuel/oxidant mixing region, whereas it occurs near the specimen surface for higher oxygen concentration. The location of gas phase reactions depends on fluid dynamics and on the transport time of the fuel/oxidant mixture. The ignition occurs from 400 s (see Fig. 7), when there is enough MMA fuel [68, 69] or other products in the gas phase to achieve the LFL (1.7% for the MMA [70]). The energy generated by the gas phase oxidation into the chimney has no direct effect on the decomposition rate of the PMMA sample (see Figs. 8a to 8c) because the flame is also far from the specimen surface. For this reason, the shapes of SMLR between tests apparatus (see Fig 8) are similar. Concerning the CACC design without chimney, a transitory combustion with flash point during the test could be observed (see Fig. 7a). When the mixture of gas and oxidant emerges from the VAC, it encounters the ambient oxidizer. The fuel mixture going out from the VAC in such condition entrains surrounding air, leading to a dilution of the combustible mixture under the LFL. A flashing ignition (equivalent to a flash point) could occur close to the igniter, but could not be maintained, as the flame is “blown” by the surrounding air before reaching a stationary state. This result induces that the CACC design without a chimney seems inappropriate to study phenomena in the gas phase under low oxygen concentrations, especially because under these conditions, the flammability region of MMA is slightly reduced (the difference between UFL and LFL). Nevertheless, it can be used to study the chemical decomposition of the solid phase, as the mass loss rate curves are comparable.

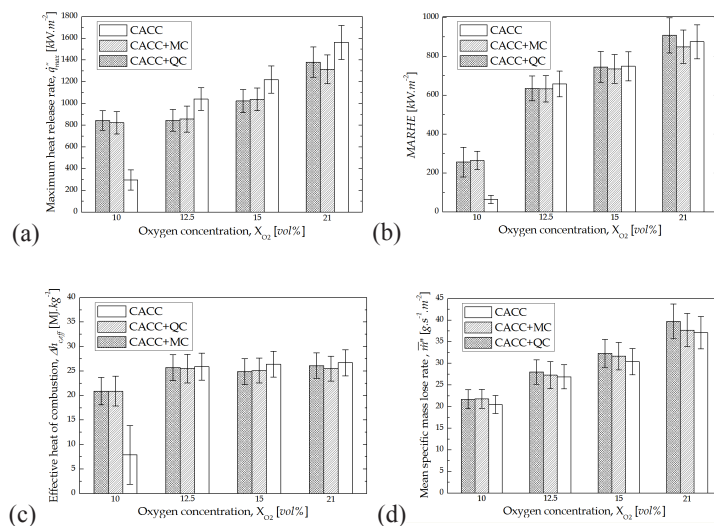


Fig. 9. Influence of test apparatus designs on (a) the maximum heat release rate \dot{q}_{max}'' , (b) the MARHE, (c) the effective heat of combustion $\Delta h_{c,eff}$ and (d) the mean specific mass loss rate \bar{m}'' . The graphs present the averaged value of three tests and their uncertainties including dispersion and analytical uncertainties. Analyses were performed a $50 \text{ kW} \cdot \text{m}^{-2}$ and for all oxygen content tested: 10, 12.5, 15 and 21 vol%.

Furthermore, the characteristics of the chimney have a significant effect on the physical and chemical processes occurring in the gas phase. For instance, the small differences observed in the HRR between the two CACC designs with QC (see Fig. 7b) and MC (see Fig. 7c) seem to be related to the thermal and optical characteristics of the chimney used,

which may favour the heat exchange and therefore the gas phase oxidation reaction. The height of the chimney also has an influence on the behaviour of the gas phase. The height must be important enough to limit the oxidation of gas past the chimney. When the height of the chimney decreases, the behaviour tends to that obtained by the CACC design. The height of the chimney proposed by Hietaniemi et al. [22, 23] or Werrel [32, 33] seems to be too small (200 mm) and the behaviour is close to those obtained by the CACC design without a chimney. As Hietaniemi et al. argue correctly, this design needs the use of an effective global equivalence ratio (Eq. 2). However, this correction proposed by the author is not necessary when the whole flame is contained in the controll volume. The use of Eq. 1 is then possible if the height of the chimney is adapted to contain all the gas phase oxidation reactions. In our experiments, this was the case with the 600 mm chimney at 10% O₂.

Figure 9 gives the average values \bar{u}_{ij} of \dot{q}_{\max}'' , the $\Delta h_{c,\text{eff}}$, the MARHE and the \bar{m}'' and their uncertainties. Uncertainty bars represent both experimental standard deviation and measurement uncertainty, with a confidence of 95 %. The results show that the accuracy of the measurement is affected at 10 vol% of O₂. A trend may be visible on analyses performed from 21 vol% down to 12.5 vol% of O₂ for the mass loss rate but no strict conclusions could be done because of experimental uncertainties. In the next section, statistical analyses were performed on the data at 10 vol% to examine their behaviour.

The aim of the statistical assessment is to investigate causality, and in particular to draw a conclusion on the effect of changes in the values of predictors or independent variables on dependent variables or response. In accordance with the standard ISO 5725 [49, 50], the analysis of the experimental data from similar tests apparatus involves two successive steps: (1) Critical examination of the data in order to identify and treat outliers; (2) Comparison and equivalence between methods. From data collected on a number of specific levels, repeatability and reproducibility, standard deviations are to be estimated. The presence of values that appears to be inconsistent with all values may change the estimates and decisions have to be made with respect to these values.

3.2.1. Scrutiny of results for consistency and outliers

The data were critically examined in order to identify outlying values and other inconsistencies. An outlier is an observation that appears to deviate markedly from other observations in the sample. Identification of potential outliers is important for the following reasons:

- An outlier may indicate bad data. For example, an experiment may not have been run correctly. If it can be determined that an outlying point is in fact erroneous, and then the outlying value should be deleted from the analysis (or corrected if possible).
- In some cases, it may not be possible to determine if an outlying point is bad data. Outliers may be due to random variation or may indicate something scientifically interesting. In any event, we typically do not want to simply delete the outlying observation.

From data collected, repeatability standard deviation is to be estimated. The values that appear to be inconsistent with the other measurement may change the estimates and decisions have to make with respect to these values. To estimate the inconsistencies of the values, both a “graphical technique” and “numerical outlier tests” were applied.

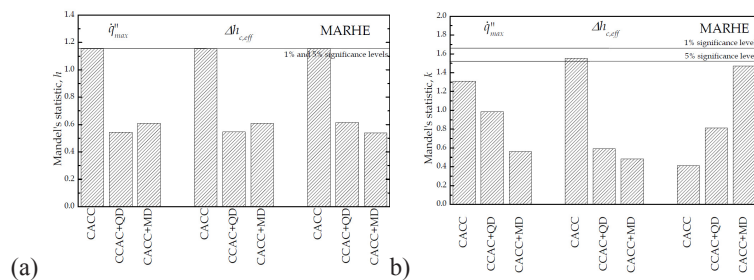


Fig. 10. (a) Mandel's between-consistency statistic, h grouped by measurement data. Values are absolute. (b) Mandel's within-laboratory consistency statistic, k grouped by measurement data. Statistical analyses were performed on PMMA at 10 vol% of oxygen and for an irradiance level of 50 kW.m⁻². The 5% and 1% significance level serve as guides when examining patterns in the data. They are given the ISO 5725 [50].

First, the graphical consistency technique was applied. Two metrics called Mandel's h and k statistics are used. Mandel's h statistic is a measure of the between-laboratory consistency while Mandel's k statistic is a measure of within-laboratory consistency [49]. In Fig. 10, the respective h and k values are plotted for each cell, grouped by measured data. The horizontal lines on the h and k plots are indicators for Mandel's h and k statistics at the 5 % and 1 % significance level. These indicator lines serve as guides when examining patterns in the data. The graphical consistency technique was applied

to the \dot{q}_{\max}'' , the $\Delta h_{c,\text{eff}}$, the MARHE values of the black PMMA at 10 vol% of oxygen. In order to support reading our graph, all h values were absolute. As can be seen in Fig. 10a, no test apparatus configuration exhibits patterns of results that are markedly different from the other apparatus in the study. No tests apparatus repeatability on the k plot (see Fig. 10b) as having significantly different values than another tests apparatus. Nevertheless, it can be seen that the value of $\Delta h_{c,\text{eff}}$ from the CACC design are outlier.

Next, numerical outlier tests such as Cochran's test and Grubbs' test were applied. The Cochran's C test is a one-sided upper limit variance outlier test [50, 70]. The C test was used to decide if a single estimate of a variance is significantly larger than a group of variances with which the single estimate is supposed to be comparable. While, the Grubb's statistic G is a statistical test used to detect outliers in a univariate data set assumed to come from normal distributions [50]. This test determines whether or not a single outlying value within a set of measurements varies sufficiently from the mean value that it can be statistically classified as not belonging to the same population, and can therefore be omitted from subsequent calculations. The tested data are the minimum and maximum values.

The calculated Cochran's statistics together with the critical values (depending on the number, p , of sets of standard deviations) are compiled in Fig. 11a while the Grubbs' statistic, as well as the critical values, are plotted in the Fig. 11b. The critical values at the 5% and 1% significance level are given in ISO 5725 [50].

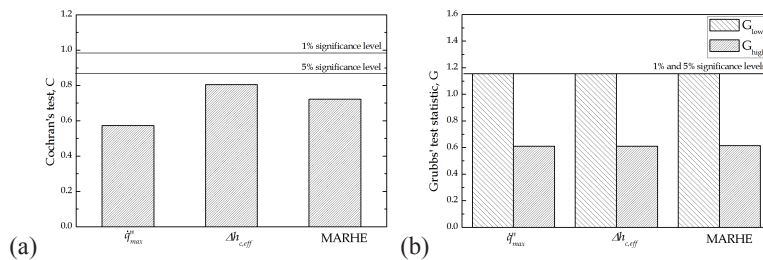


Fig. 11. (a) Application of the Cochran's test statistic C to cell variances. (b) Application of the Grubbs' test to cell mean. Analyses were performed on PMMA at 10 vol% of oxygen and for an irradiance level of $50 \text{ kW}\cdot\text{m}^{-2}$. The 5% and 1% significance level serve as guides when examining patterns in the data. They are given in ISO 5725 [50].

When the test statistic is less than or equal to its 5% threshold value, the item tested is accepted as "correct". Upon application of Cochran's test and Grubbs' statistics, no stragglers or outliers between values were detected for tests with an oxidizer of 10% oxygen. The values of C and G are lower than their 5% threshold values. This analysis of the Cochran test shows that the within laboratory variance is similar between tests apparatus. The Grubbs' test reveals that the average value of each test is not significant compared to the mean value of all apparatus. The Cochran and Grubbs criteria test only the highest or lowest values in a set of standard deviations and are therefore one-sided outlier tests. Great caution should be exercised before drawing conclusions and therefore a closer examination seems to be necessary.

3.2.2. Comparison and equivalence between methods

The analysis of variance (ANOVA) methods are a common practice to demonstrate the equivalence of a measurement method. The principle consists in comparing the mean value and the variance.

First, the variances are statistically compared with Fisher's test of equality of variance also known as the F-test [71]. The aim of this analysis is to estimate if these variances can be considered identical or not. The F-test can be regarded as a comparison of two variances, but the specific case being discussed in this article is that of two populations, where the test statistic used is the ratio of two sample variances. Let X_1, \dots, X_n and Y_1, \dots, Y_m be independent and identically distributed samples from two populations which each have a normal distribution. Let s_X^2 be the sample variance of X_1, \dots, X_n and s_Y^2 those of Y_1, \dots, Y_m . Under the hypothesis that the variances are equal, the F-test statistic is defined as defined in Eq. (12):

$$F_{\text{observed}} = s_X^2 / s_Y^2 \quad (12)$$

with $s_1 > s_2$ so that $F_{\text{observed}} > 1$. In this test, the ratio of the two variances (F_{observed}) is then compared to a theoretical F-ratio (F_{th}). The F_{th} value is given in the Fisher-Snedecor table. In our case, the F_{th} threshold value is equal to 19.

F_{th} values are tabulated for different levels of probability.

- If $F_{\text{observed}} < F_{th}$, then the variances are regarded as equal,

- If not, they are significantly different.

Next, the mean values are statically compared with the student's T-test [72]. A T-test is any statistical hypothesis test in which the test statistic follows a Student's t distribution if the null hypothesis is supported. This test is used only when it can be assumed that the two distributions have the same variance. Let \bar{u}_X and \bar{u}_Y the mean value of series X and Y , while n_x and n_y are the number of repetitions of series X and Y . The T statistic to test whether the means are different can be calculated as defined in Eq. (12)

$$T_o = |\bar{u}_X - \bar{u}_Y| \left[\frac{(n_x - 1)s_X^2 + (n_y - 1)s_Y^2}{n_x + n_y - 2} \sqrt{\frac{1}{n_x} + \frac{1}{n_y}} \right]^{-1} \quad (13)$$

This value is compared with the value of the Student's table at a degree of freedom $n = n_1 + n_2 - 2$.

- If $T_o < T_{students}$, the mean values are regarded as equal.
- If not, they are significantly different.

The ANOVA methods were applied on the data of \dot{q}_{max}'' , the $\Delta h_{c,eff}$ and the MARHE at 10 %vol of oxygen. Fig. 12a presents the analysis on the variance (following the F-test) while the Fig. 12b gives those on the mean value (T-test).

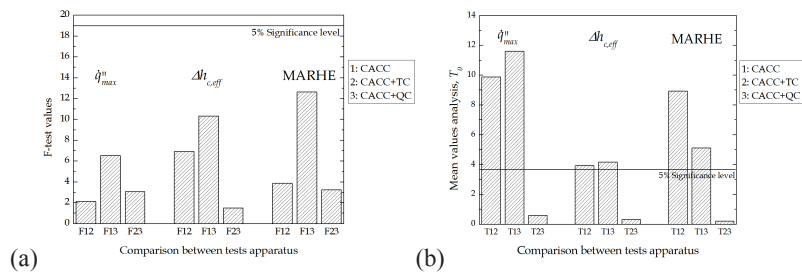


Fig. 12. (a) Comparison of variance from F-test. (b) Comparison of mean value. Analyses were performed on PMMA at 50 kW.m⁻² for all oxygen contents tested: 10 vol%. The number 12 (23 or 32) defines the comparison between the test benches 1 and 2 (1–3 or 2–3) for instance. The index 1 characterizes the CACC apparatus, while the 2 is the CACC with a metallic chimney and the 3 is the CACC with a quartz chimney. The 5% significance level serves as guides when examining patterns in the data.

Analysis on the variance shows effects of test bench designs. The values F_{12} and F_{13} are higher than the Fisher threshold variable. This result explains that the use of a specific design may affect the accuracy and repeatability of measurement.

Furthermore, the mean value analysis (see Fig. 12b) reveals significant deviations between the CACC design with (2 & 3) and without chimney (1). The values t_{12} and t_{13} are higher than the Student threshold variable. Thereby, this remark suggests that the designs are not similar and the reaction-to-fire of polymer materials and the test accuracy are strongly dependent on the design used. In contrast, the t_{23} value is lower than the Student threshold variable: Hence, in this configuration, there is no influence of the design on the test results.

For each test, the two series of results are equivalent if the variances and the means are found to be statistically equal. Therefore, this analysis also confirms that it is not possible to discern differences in the results for designs with and without a chimney. Without statistical analyses, strictly proven conclusions and confirmation of assessment could not be made.

4. Conclusions

The flammability of materials is of intense interest in fire safety research. Over the last few years, non-standard research devices capable of evaluating the reaction-to-fire of materials under non-ambient oxygen conditions have been developed. One such device is the *controlled atmosphere cone calorimeter* (CACC). Until now, this test method has not been standardized and the design can change from one testing laboratory to another. This modification can affect the measurements and also its accuracy.

In the present paper, we have studied the vitiated air enclosure influence on measurement accuracy. The experimental analyses were performed under ambient and non-ambient oxygen conditions. Four designs were further investigated using a Poly(methyl)methacrylate (PMMA) material. Statistical analyses were performed in some cases to examine the relevance of the data. Investigations were carried out following the same test protocol to check the repeatability and reproducibility between test apparatus. The accuracy and precision of the test apparatus were assessed by means of the standard ISO 5725.

Under ambient oxygen conditions, it was shown that there is no significant deviation in the accuracy and repeatability of measurements between test apparatus, given their experimental uncertainties. Nevertheless, further work is needed on other materials to confirm this trend.

Under non-ambient oxygen conditions, the analyses have shown that the design has a great influence on the reaction to fire of polymer and its measurement accuracy, mainly at 10 vol% of oxygen. From 21 vol% down to 12.5 vol% of oxygen, the gas phase oxidation is more important in the CACC design without a chimney. At 10 vol% oxygen, this behaviour changes radically and the use of a chimney modifies the kinetics of the heat release and the oxidation of gaseous species. Nevertheless, a statistical analysis shows that there is no influence between the designs for the chimney studied.

We may conclude that the definition of a standard design seems to be necessary to assure a harmonization of analyses. In the case of CACC without direct connection with the exhaust hood, the CACC design without a chimney seems to be inappropriate to study phenomena in the gas phase under low oxygen concentration. Nevertheless, it can be used to study the chemical decomposition of the solid phase. The dependency of the chimney dimensions has not been studied yet. However, its height must be important to limit oxidation of gas past the chimney.

Further work is needed to define the design most adapted to predict the fire behaviour of polymer material under non-ambient atmosphere conditions.

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