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The Controlled Atmosphere Cone Calorimeter: A Literature Review

*Robert John Bray**, *Belfast School of Architecture and the Built Environment, Ulster University, Belfast BT15 1AP Northern Ireland, UK and Hydrock Consultants Ltd, Merchants House North, Wapping Road, Bristol BS1 4RW, UK*

Svetlana Tretsiakova-McNally and Jianping Zhang, Belfast School of Architecture and the Built Environment, Ulster University, Belfast BT15 1AP Northern Ireland, UK

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Abstract. Cone calorimeters are widely used to assess heat release parameters and flammability of combustible materials, but their use is limited for applications where the global equivalence ratio (GER) exceeds one, because they can only replicate burning in open conditions. The standardisation of the controlled atmosphere cone calorimeter (CACC) in the ISO/TS 5660-5:2020 offers an opportunity to investigate the potential advantages and limitations of this apparatus. This paper presents a detailed review of existing studies conducted using the CACC. The review is aimed at examining the importance of atmospheric control for bench-scale experimental methods and the research-based development of key features of the apparatus. In addition, it highlights the research yet to be carried out to optimise the use of CACC as a tool in fire science. The effects of various design parameters are discussed including the method used for GER control, the chimney, the chamber, the gas inflow rate and others. Despite standardisation, it is concluded that there is limited consensus on optimal CACC control variables. A lack of consensus has led to significantly different testing conditions even where researchers use the same materials and have similar research objectives. The lack of best practice, particularly with regards to a gas sampling location and the method of GER control, motivates the need for further research so as to improve the value of data collected, reduce uncertainty and optimise CACC reproducibility.

Keywords: CACC, Cone calorimetry, Controlled atmosphere, Equivalence ratio, Under-ventilated conditions, Vitiated conditions, Toxicity

List of Symbols

ϕ	Equivalence ratio (N/A)
$\dot{m}_{fuel}$	Mass loss rate of fuel (g/s)
$\dot{m}_{oxygen}$	Mass flow rate of oxygen (g/s)
ϕ_{GER}	Global equivalence ratio (N/A)
$X^{E}_{O_2}$	Oxygen concentration in the enclosure (N/A)

*Correspondence should be addressed to: Robert John Bray, E-mail: bray-r@ulster.ac.uk

$\dot{m}_g^E$	Mass flow rate of the incoming gas mixture to the enclosure (g/s)
$\dot{m}_{O_2,eff}(t)$	Oxygen mass rate, effective value (instantaneous value) (g/s)
$\dot{m}_{O_2,in}(t)$	Controlled oxygen mass feeding rate (instantaneous value) (g/s)
$\dot{m}_{O_2,consumed}(t)$	Rate of oxygen consumption (instantaneous value) (g/s)
t_{ig}	Time to ignition (s)

Abbreviations

CC	Cone calorimeter
HRR	Heat release rate
MLR	Mass loss rate
EHC	Effective heat of combustion
CO	Carbon monoxide
CACC	Controlled atmosphere cone calorimeter
FPA	Fire propagation apparatus
MaCFP	IAFSS Working Group on Measurement and Computation of Fire Phenomena
CO_2	Carbon dioxide
GER	Global equivalence ratio
THE	Total heat evolved
PMMA	Poly(methyl methacrylate)
ABS	Acrylonitrile butadiene styrene
PE	Polyethylene
PS	Polystyrene
PP	Polypropylene
PIR	Polyisocyanurate
PVC	Polyvinyl chloride
HCN	Hydrogen cyanide
FT-IR	Fourier-Transform Infrared Spectroscopy
PUR/PUF	Polyurethane
GC	Gas chromatography
MS	Mass spectrometry
TTI	Time to ignition
HCl	Hydrogen chloride
NO_2	Nitrogen dioxide
PCO	Post chamber oxidation
PHRR	Peak heat release rate
THC	Total hydrocarbon
RSM	Response surface methodology
SSTF	Steady state tube furnace
ELSA	Equivalent low stretch apparatus
LC50	Lethal concentration 50%

1. Introduction

The cone calorimeter (CC) was initially used for the determination of properties necessary for the assessment of fire hazard and is a widely used and well-established experimental method in fire safety engineering. It has previously been the focus of comprehensive review [1], and will only be discussed briefly here. Typically, properties of interest comprise of heat release rate (HRR), mass loss rate (MLR) and effective heat of combustion (EHC). The open design of the CC ensures that a conservative estimation of these properties is obtained by exposing samples to a heat flux representative of a smoke layer in a protracted enclosure

fire whilst maintaining a ready supply of fresh air to the sample. Whilst CC conditions are preferable for inducing conservative approximations of fire load and flammability, using the CC to produce toxicity data, another integral consideration necessary for assessment, does not guarantee the identification of optimally hazardous conditions. Although the CC can be used to collect smoke and toxic species, the value of this data is considered unrepresentative of worst-case conditions in compartment fire scenarios [2]. There is now research consensus that the CC is inappropriate for collecting species yields representative of under-ventilated fire conditions. Whilst it is thought that engineering predictions and correlations could eventually overcome this deficiency [3], this is not yet the case.

It has been suggested that since the HRR is the primary factor controlling toxic species production there is a limited need for toxicity risk measurement methods, and by extension bench-scale methods for collecting such data, in building regulations [4]. Despite this assertion, there has been a growing interest in the investigation of toxic products formed in oxygen depleted conditions typical for under-ventilated, or ventilation controlled, fires. These conditions are considered to present the highest level of toxic hazard by virtue of the greater volume of fire effluent, due to fire growth that proceeded oxygen depletion, as well as the greater yields for most toxic species responsible for fire deaths [5]. There has been a focus on developing a bench-scale method for toxicity evaluation that is capable of measuring a range of enclosure fire growth stages due to the higher costs and complexity of large-scale testing. However, the use of toxicity measurements for the assessment of building materials is currently limited in part because it has proven challenging to develop a reliable method capable of replicating toxic yields found in large fires [6]. For example, a lack of confidence in carbon monoxide (CO) measurements varying by two orders of magnitude between tests for common fuels has led to the removal of CO exposure criterion from all but smouldering design fires in Australian performance-based design guides, as reported in [6]. Stec [5] believes that further development of an apparatus capable of measuring fire toxicity will increase the interest in the subject and will promote a recognition of the risks of toxic species not yet addressed.

Subsequently, there is a desire to facilitate control of atmospheric conditions to which materials are exposed [7] so that the worst-case conditions, for certain fire properties, can be examined. The controlled atmosphere cone calorimeter (CACC) is one such apparatus capable of controlling a wider range of variables necessary for simulating oxygen depleted conditions and has been said to offer a promising method of obtaining suitable data for hazard and risk analysis [8]. The CACC has also been identified as an important alteration to experimental methods when faced with changing energy performance requirements within the housing sector in Europe and the resulting impact these changes may have on fire behaviour [9]. It is uncertain how the increased insulation properties of a more energy efficient built environment may affect the onset of ventilation-controlled conditions, as well as our emphasis on simulating them. However, should a consequence be an increase in oxygen deficient enclosure fires more rigorous methods of determining fire properties in these conditions will be necessary.

The scope and use of the CACC are varied and, with standardisation only occurring in 2020 [10], are in their infancy. As an adaptation to one of the most widely used methods of collecting experimental data for fire safety engineering, described as a potential basis for more realistic toxicity and smoke obscuration test standards [11, 12], there is a significant value in further review. The purpose of this review will, therefore, be to investigate the literature available on the CACC to characterise some of its key components as well as the limitations in its use. To the authors' knowledge, there has been no comprehensive study on the CACC apparatus to date.

The present article summarises research into the key features of the CACC including the chamber inflow rate, the chimney design and the calculation methodology of HRR. These features were identified as the primary issues for apparatus development in a 2015 workshop on the CACC [13]. CACC designs might have numerous differences but can be broadly categorised as either open-CACCs or closed-CACCs. Open-CACCs have no connection between the combustion chamber and exhaust hood, whereas the chamber directly connects in the case of the closed-CACC. A schematic of a standardised open-CACC [10] is shown in Figure 1. Prior to ISO/TS 5660-5 [10] standardisation, research often featured significant dissimilarities in experimental protocol and apparatus design. These dissimilarities make interpretation of data more challenging and were one of the main drivers for defining an internationally agreed design standard. This review presents a non-exhaustive comparison of the main differences in apparatus design reported between 1991 to 2022.

2. Literature Overview

A total literature body was collected, primarily from searches on Google Scholar, consisting of 69 research papers. The search terms were ''Controlled atmosphere cone calorimeter'', ''Modified cone calorimeter'', ''Vitiated cone calorimeter'' and ''Controlled ventilation cone calorimeter''. These works date from 1991 to 2022. Best efforts have been made by the authors to provide a complete study into this topic. Research primarily made use of the CACC as a tool for determining fire properties associated with flammability, calorimetry or toxicity. In some unique cases the CACC was used to assess the corrosivity of electrical components exposed to fire effluent [14], the assessment of the thermal degradation of intumescent coatings [15], a study into chemical analysis techniques used to investigate fire debris [16], the ignition times of fuels located within oxygen reduction systems [17] and the evaporation rates of liquid fuels [18] as well as others.

2.1. Chamber Atmosphere

The CACC allows for three methods of controlling the atmosphere within the sample chamber. Firstly, the user can use a mixture of air and an inert gas (a diluent), at a ratio that lowers the volume percent of oxygen (O_2) within the chamber, with an inflow rate sufficiently high to prevent additional under-ventilation. The necessary inflow rate to prevent under-ventilation is dependent on the

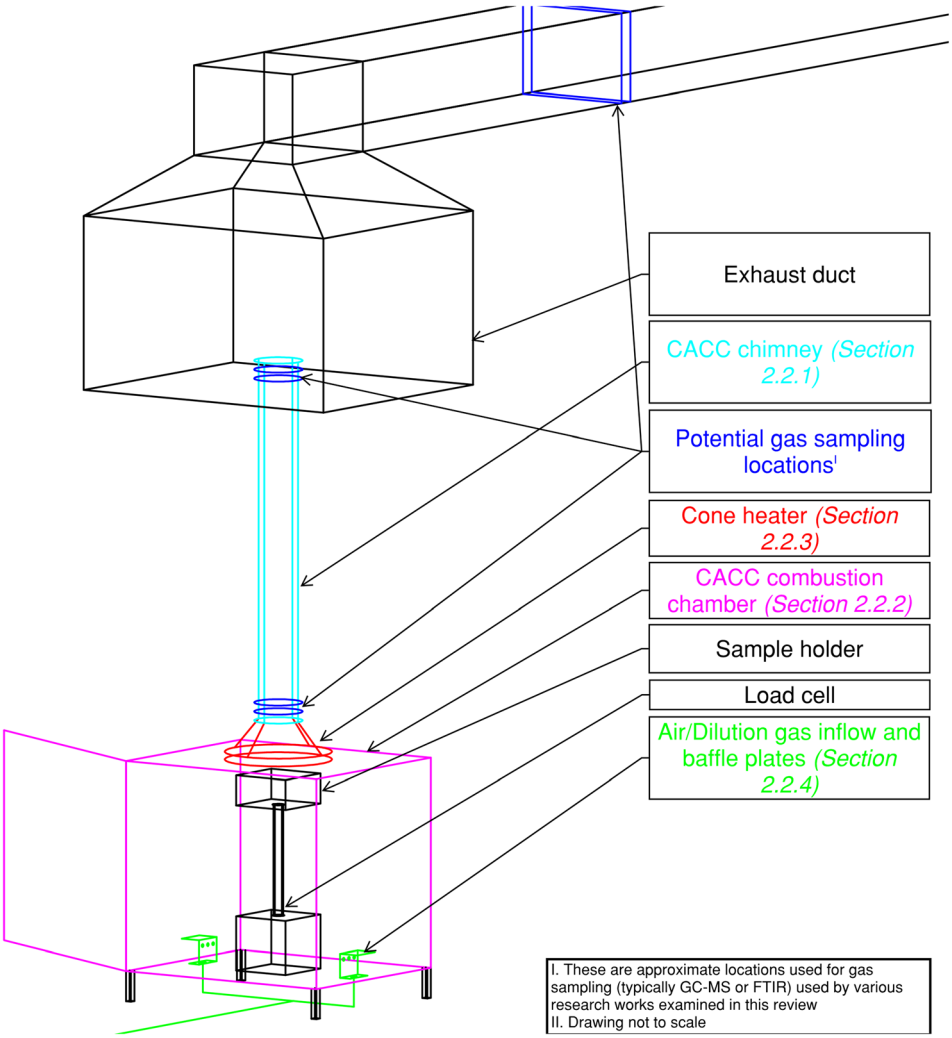

Figure 1. Open-CACC design.

calorific output of the fuel but a flow rate of 150 to 180 L/min was recommended in [10] based on earlier research [19]. The inert gas is usually nitrogen (N_2) but carbon dioxide (CO_2) has also been used. Alternatively, no inert gas is mixed into the inflow and the total mass flow rate of air can be reduced to create under-ventilated conditions. For under-ventilated tests the inflow rate should not fall below 10 L/min according to ISO/TS 5660-5 [10], although research using flow rates of 6 to 100 L/min [9], 20, 21 have been reported. A third option is to use a combination of the two previous methods by lowering both the flow rate and mixing air with a diluent gas. This is an uncommon approach that has not been researched widely partly because the introduction of both methods makes it harder to discern

the cause of the changes observed [9]. However, work coupling these methods has produced CO/CO_2 ratios that do not vary considerably as oxygen concentrations are reduced [22], indicating notable differences from typical findings under exclusively vitiated conditions [2].

There is no consensus at this stage for operating conditions that are preferable for one of the primary uses of the CACC, namely for the collection of toxic effluent data. For example, recent research into the collection of toxic data for wood species at 50 kW/m^2 has used both under-ventilated flow rates of 6 to 28 L/min [21, 23, 24] and vitiated flow rate of 144 L/min [25]. This decision is, however, critical to the toxic species data collected, the conditions replicated, and the challenges faced for apparatus design. The exploration of material decomposition in reduced oxygen environments is not well understood partly because of the limited number of studies focussing on this topic [26]. Further to this, the consideration of how oxygen reduction is introduced is not always well defined within the studies themselves.

2.1.1. The Equivalence Ratio The equivalence ratio (ϕ), as defined in Equation 1, is frequently used to compare results between different experimental apparatus and scales. The value of ϕ allows flaming conditions to be characterised by a term that, during flaming combustion, has a significant effect on species yields in the fire effluent [27]. In some cases, standardised tests specify values for ϕ that correspond to different fire stages. For example, for the steady-state tube furnace (SSTF) well-ventilated conditions are characterised as $\phi \leq 0.75$, whilst under-ventilated conditions as $\phi = 2 \pm 0.2$ [28]. Although the principle was originally used in combustion science to describe localised conditions, it has also been used to describe conditions of a system more generally, often called the global equivalence ratio (GER) [27]. Whilst the equivalence ratio refers to the mass ratio of fuel to oxygen divided by the stoichiometric equivalent, the global equivalence ratio is often defined by a mass flow into a control volume. This global term does not account for localised fluctuations within the control volume and thus can only be considered meaningful when there is limited uncertainty from spatial and temporal variation in the control volume, such as under well mixed conditions. Typically, fires with $\phi_{GER} > 1$ are considered fuel-rich whilst $\phi_{GER} < 1$ are fuel-lean [23]. The calculation of ϕ_{GER} in ISO/TS 5660-5:2020 [10], as shown in Equation 2, allows for comparison between under-ventilated and vitiated test conditions using similar values of ϕ_{GER}, despite the different chamber inflow rates. Calculation of ϕ_{GER} has also been used to ensure that chamber inflow rate does not simultaneously promote vitiation and under-ventilation during testing [29]. It is worthwhile to note that the local equivalence ratio can vary significantly to that of the GER due to the variability of oxygen concentration and flow fields. This is particularly true for the large-scale tests with a larger surface area of fuel [30].

$$\phi = \frac{\left(\dot{m}_{fuel}/\dot{m}_{oxygen}\right)}{\left(\dot{m}_{fuel}/\dot{m}_{oxygen}\right)_{stoi}} \tag{1}$$

$$\phi_{GER} = \frac{\left(\dot{m}_{fuel}/\dot{m}_g^E \cdot X_{O_2}^E\right)}{\left(\dot{m}_{fuel}/\left(\dot{m}_g^E \cdot X_{O_2}^E\right)\right)_{stoi}} \tag{2}$$

It has been reported that the GER value over-predicts oxygen consumption, when the mass flow of oxygen into the chamber is used as $\dot{m}_{oxygen}$, due to flaming above the open-CACC chimney [31]. In an attempt to compensate for the flaming effect, Hietaniemi et al. [31] proposed the use of a chimney alongside an effective global equivalence ratio, described in Equation 3. Equation 3 restricts the mass flow rate of oxygen used for combustion to the mass inflow rate of oxygen when it exceeded the mass inflow rate of oxygen during the test.

$$\dot{m}_{O_2,eff}(t) = \begin{cases} \dot{m}_{O_2,in}(t) & if\ \dot{m}_{O_2,consumed}(t) < \dot{m}_{O_2,in}(t) \\ \dot{m}_{O_2,consumed}(t) & otherwise \end{cases} \tag{3}$$

Similarly to [31], Blomqvist et al. [32] used the mass flow rate of oxygen into the chamber to describe $\dot{m}_{oxygen}$ but, alternatively, only used the O_2 mass consumption rate to calculate ϕ_{GER} where combustion occurred exclusively within the chamber resulting in a ''theoretical temporal global equivalence ratio'' and the ''effective equivalence ratio'', respectively. Blomqvist et al. [32] found large differences between GER values using different ratio calculation methods. As with Hietaniemi et al. [31] this was attributed to significant burning above the chimney leading to the creation of ''semi-well-ventilated'' conditions and resulted in the ''*effective equivalence ratio*'' displaying a lack of sensitivity to imposed vitiated conditions (in their case 15 vol% O_2 [32]). Blomqvist et al. [13], 32 suggested that the vitiated method of oxygen reduction within the CACC chamber may be unable to adequately reach high equivalence ratios.

For materials with well-defined chemical compositions, the fuel to oxygen ratio for complete combustion can often be determined from the balanced chemical equations. However, for the composite or hybrid materials, with unknown chemical formulae, elemental analysis is necessary to determine the $\dot{m}_{fuel}/\dot{m}_{oxygen}$. It should be noted though, that the results of elemental analysis may not truly represent the sample's makeup, particularly when multiple materials are present in a layered system. This uncertainty prompted Barton et al. [29] to use a ''*realistic maximum global equivalence ratio*'' featuring a $\left(\dot{m}_{fuel}/\dot{m}_{oxygen}\right)_{stoi}$ value for a known fuel, methane, in lieu of an accurate $\left(\dot{m}_{fuel}/\dot{m}_{oxygen}\right)_{stoi}$ value for the fuel itself, thereby offering conservative approximations of GER for many fuels. The CO/CO_2 ratio is also often reported and considered as an important tool for assessing CACC ventilation conditions [22, 32] and is sometimes used as an alternative to GER.

2.1.2. Chamber Atmosphere—Vitiated Conditions An abridged summary of published vitiated research using the CACC can be seen in Tables 1 and 2 for closed and open CACCs respectively.

Table 1
Literature Summary for Vitiated Tests Using A Closed CACC

References	Material type/ thickness	Irradiance (Kw/m^2)	Diluting gas and System flow rate	Oxygen concentration (vol% O_2)	Gas analysis type and location	Chamber dimensions and insulation	Load cell cooling and insulation
Mulholland et al. 1991 [33]	Methane, propane, 6 mm PMMA & PE, 13 mm ABS & Douglas fir	15, 20, 25, 30, 40, 50	Dilutant flow (either CO_2 or N_2) up to 4 L/s. Mixed inflow stream of 3 cm/s. Uses glass bead bed	14, 15, 16, 17, 21	Non-dispersive infrared analyser at the exhaust duct	Cubic with 50 cm sides. Chamber formed of pyrex	Water-cooled shutter. Load cell located outside of the chamber
Christy et al. 1995 [2]	10 mm PMMA and two 25 mm PIR foams	50	Air and N_2 mix at 9, 15 and 24 L/s ± 0.3 L/s Uses a 75 mm deep glass bead bed	(15, 18 and 21) ± 0.3	O_2, CO, CO_2 and HCN gas analysis in the exhaust duct	Double walled stainless-steel with water cooled channels. Internal walls are painted black	Load cell within chamber but rotated away from the cone until test start
Hshieh et al. 1995 [34]	Various 1 mm flame retardants or untreated fabrics	25	N_2/O_2 mix at ~ 24 L/s	(15, 18, 21, 25.9, 30) ± 0.05	Sampling method and location not reported	Not reported	Not reported
Leonard et al. 2000 [35]	PMMA and wool carpet	Not reported	N_2/air mix 0 to 30 L/s Used a 50 mm deep glass bead bed	Not reported	CO/CO_2 analysers in exhaust duct	Primarily formed of toughened glass with silicone rubber seals	Load cell located within the chamber. Cooling water pipe adjacent to hood
Hshieh et al. 2003 [36]	~ 50 to 60 mm Polyester foam	t_{ig}—55, 75 Yields—25, 35, 45	N_2/O_2 mix at ~ 24 L/s	21	CO/CO_2 analyser	Not reported	Not reported

Table 1 continued

References	Material type/ thickness	Irradiance (Kw/m^2)	Diluting gas and System flow rate	Oxygen concentration (vol% O_2)	Gas analysis type and location	Chamber dimensions and insulation	Load cell cooling and insulation
Griffin et al. 2005 [15]	3 to 5 mm steel with intumescent coating	90	N_2 and air mix. Flow rate not reported	8 to 10, 21	As reported in Leonard et al. [35]	As reported in Leonard et al. [35]	Holder made from 18.7 mm thick calcium silicate board
Gann et al. 2020 [30]	Particleboard Cotton-polyester fabric over PE foam Copper wire insulated with nylon and PVC	25, 50	12.5, 25 L/s Dilution gas likely N_2 as reported in [37]. Gases mixed in chamber before entering via 4 sets of 5 holes on each wall	14, 16, 18, 21	Non-dispersive infrared analysers for CO_2 and CO with FTIR sampling for other species. Upstream of exhaust, centreline in exhaust duct [37]	Chamber measures 430 × 500 × 570 mm high. Formed of a hollow aluminium frame with polycarbonate walls. Aluminium foil positioned in areas of high heat flux [37]	Load cell located in chamber. No method of cooling was reported
Beji et al. 2021 [18]	250 ml n-heptane and methanol depth of 25 mm in at 100 × 100 mm square stainless steel pan	25, 50	145 ± 5 L/min Air and N_2 mix 2 × inlet ports (Ø20mm) on floor	~ 2 to 5	None (investigated evaporation rates and liquid temperatures)	Chamber measures 383 × 326 × 330 mm high	Cooling around load cell stem. 26 mm thick gypsum board was positioned above the load cell[a]

[a]Three 50 × 100 mm air vents in the board maintained chamber conditions. The sample pan also included calcium silicate insulation of 57 mm (underside) and 18 mm (sides)
[b]To provide a concise summary of the available literature a number of articles have been removed from this table including (Petrella, 1994) [38] (Hshieh, 1997) [39] (Hshieh, 1997) [40] (Dowling, 1999) [41] (Hshieh, 2002) [42] (Alibert, 2017) [43] (Alibert, 2019) [44]

Table 2
Literature Summary for Vitiated Tests Using an Open CACC

References	Material type/thickness	Irrad. (Kw/m^2)	Diluting gas and inflow rate (L/min)	Extract fan flow rate (L/s)	Oxygen concentration (vol% O_2)	Type of chimney	Gas analysis type and location	Chamber dimensions and insulation	Load cell cooling and insulation
Mikkola 1993 [45]	50 mm PS, PP and Nylon, PVC[a], 11 mm particleboard, 6 mm black PMMA	50	Air/N_2 mix 90 to 480	3, 6	15, 21	"short" chimney	FTIR at the exhaust duct	Junction between chamber and cone heater is water cooled	Load cell inside chamber
Marquis et al. 2011 [46]	Sandwich panel of balsawood and laminate polyester resin	20, 35, 50	Air/N_2 mix [b] 2× inlet ports on side wall	Not reported	0, 5, 10, 15, 23	Quartz chimney	FTIR sampled at the exhaust duct	Not reported	Load cell located outside of chamber
Marquis et al. 2013 [47]	14 mm PIR foam	50	Air/N_2 mix 160 ± 5 2× gas inlet ports on floor	24	0, 5, 10, 15, 21	Metal 60 cm long chimney	FTIR via ring probe at chimney exit. CO, CO_2 & O_2 analysers	Stainless-steel with front window. Water cooled between chamber and cone	Load cell inside chamber
Marquis et al. 2013 [19]	14 mm PMMA	20, 35, 50	Air/N_2 mix 160 ± 5 2× inlet ports on floor	24	10, 12.5, 15, 21	Compares no chimney, and 60 cm quartz/metal chimneys	FTIR via ring probe at chimney exit. $CO/CO_2/O_2$ analysers from exhaust duct	Stainless-steel with front window. Water cooled between chamber and cone	Load cell inside chamber

Table 2
continued

References	Material type/thickness	Irrad. (Kw/m^2)	Diluting gas and inflow rate (L/min)	Extract fan flow rate (L/s)	Oxygen concentration (vol% O_2)	Type of chimney	Gas analysis type and location	Chamber dimensions and insulation	Load cell cooling and insulation
Hermouet et al. 2014 [48]	30 mm PIR foam	20, 35, 50	Air/N_2 mix 2× inlet ports on floor	Not reported	0, 5, 10, 15, 21	60 cm long stainless-steel chimney	FTIR sample at the exhaust duct CO/CO_2/O_2 analysers from exhaust duct	As described in Marquis et al. [47]	As described in Marquis et al. [47]
Marquis et al. 2014 [49]	14 ± 1 mm black PMMA	50	Air/N_2 mix 100 (± 5), 130 (± 7), 160 (± 5) 190 (± 7) 2 × inlet ports on floor	24	0, 5, 10, 12.5, 15, 21	60 cm chimney	CO, CO_2 and O_2 analysers within the exhaust duct	As described in Marquis et al. [47]	As described in Marquis et al. [47]
Werrel et al. 2014 [7]	Black PMMA and particleboard	15, 25, 50, 75	Air/N_2 150 2× inlet ports on floor	12, 15, 18, 24	15, 17, 18, 19, 21	18 cm in length Ø8 cm chimney	Sampling taken from the exhaust duct 40 × 40 × 40 cm	Stainless steel enclosure of about Load cell inside chamber	
Marquis et al. 2017 [26]	30 mm PIR foam	20, 35, 50	Air/N_2 mix 160 ± 5 2× inlet ports on floor	24	0, 5, 10, 15, 21	60 cm metallic chimney	FTIR via a ring probe at the top of the chimney. Thermocouples also located in chimney. CO/CO_2/O_2 analysers from exhaust duct	Stainless steel CACC chamber dimensions 38 × 32 × 35 cm^3	As described in Marquis et al. [47]

Table 2 continued

References	Material type/ thickness	Irrad. (Kw/ m^2)	Diluting gas and inflow rate (L/min)	Extract fan flow rate (L/ s)	Oxygen concentration (vol% O_2)	Type of chimney	Gas analysis type and location	Chamber dimensions and insulation	Load cell cooling and insulation
Blomqvist et al. 2018 [13]	10 mm black PMMA and various 50 mm insulation types	50	Air/N_2 mix 160 ± 5	24	10, 15, 18, 21	60 cm stainless-steel chimney with Ø80 mm	FTIR sampled in exhaust duct using a stainless-steel probe with a single opening	Metal chamber dimensions were 380 mm (w) × 320 mm (d) × 340 mm (h)	Load cell not water cooled. Load cell located in chamber
van Hees et al. 2018 [17]	10 mm thick particle board for HRR tests 12 mm clear PMMA for ignition times	25, 50 (HRR) 18, 35 (t_{ig})	Air/N_2 mix 160	24	15, 21 (HRR) 16, 21 (t_{ig})	CACC without chimney compared to CACC with 30 cm long chimney with Ø10 cm	Not reported	Not reported	Load cell within chamber
Knez et al. 2021 [25]	20 mm thick Spruce, Particleboard, and oriented strand board	50	Air/N_2 mix 144 L/min Inlet port on CACC chamber sidewall	Not reported	10, 15, 21	500 mm long chimney	Sampled at chimney exit. Effluents captured using glass wool filters and PUR plugs. Analysed using GC–MS	CACC measures 37 × 33 × 30 cm	Load cell located in chamber. No method of cooling reported

Table 2
continued

References	Material type/thickness	Irrad. (Kw/m^2)	Diluting gas and inflow rate (L/min)	Extract fan flow rate (L/s)	Oxygen concentration (vol% O_2)	Type of chimney	Gas analysis type and location	Chamber dimensions and insulation	Load cell cooling and insulation
Barton et al. 2021 [29]	Mineral oil in the bottom half of a specimen holder and 5 mm deep Two cable types with outer diameters of 9.5 and 5 mm	20, 30, 50	120, 150 2× inlet ports on floor	24	13, 14, 15, 17[c]	600 mm long chimney with a Ø115 mm	$CO/CO_2/O_2$ analysers sampled in the exhaust duct	Stainless-steel chamber (386 × 326 × 350 mm height) with an observation window at the front. Junction between chamber and cone heater is water cooled	Load cell located within the chamber

[a]PP, PS and nylon samples are in pellet form. PVC is in powder form
[b]An oxygen and air mixture is reported which is assumed to be an error
[c]Tests were also performed at 21 vol% O_2 but used a cone calorimeter
[d]To provide a concise summary of the available literature a number of articles have been removed from this table including (Gomez, 2010) [50] (Gomez, 2011) [51] (Hermouet, 2014) [52] (Hermouet, 2015) [53] (Hermouet, 2021) [54] (Mun, 2021) [55] (Bray, 2021) [56]

Heat Release Rate, Mass Loss Rate and Effective Heat of Combustion—For many early research papers, the HRR or EHC obtained through open-CACCs using vitiated conditions, as given in Table 2, were calculated based on ISO 5660-1 [57], using the oxygen consumption principle [58]. This method has been shown to overpredict the HRR, particularly in conditions with low oxygen concentrations, and as a result produced incorrect values for EHC [7]. Werrel et al. [7, 59] presented a modified calculation approach that considered incomplete combustion by the generation of CO. Their results using the original calculations in ISO 5660-1 [57], illustrated in Figure 2, show a misleading trend whereby the Total Heat Evolved (THE) was shown to rise in vitiated conditions. The corrections to the calculation procedure proposed by [7], now included in ISO/TS 5660-5 [10], report that THE had no dependence on oxygen concentration as would be expected.

Research has broadly reported that vitiated conditions reduce HRR and MLR [60]. Typically, neither have been shown to decrease at a constant rate as the oxygen concentration is reduced [17], although the reduction of MLR has been described using a linear function of the oxygen concentration for a range of fuels [61]. Christy et al. [2] found that the MLR and HRR for PMMA and polyisocyanurate (PIR) foams decreased when the oxygen concentration was reduced from 21 vol% to 15 vol%. However, they concluded that the EHC was independent of vitiated conditions due to extended time to extinction observed at lower oxygen concentrations [2]. For polystyrene (PS) and PMMA, Petrella found that vitiation (15.3 to 21 vol% O_2) reduced peak HRR but had a negligible effect on time to ignition (TTI) and EHC [38]. Chatenet et al. [22] found that the TTI increased whilst peak MLR, peak HRR and EHC decreased as oxygen concentration decreased for PMMA samples during flaming combustion, but that peak MLR remained stable where the sample failed to ignite ($\leq$9 vol% O_2). Despite Chatenet et al. [22] using a combined vitiated and under-ventilated method, PMMA MLR and HRR decreased linearly as oxygen concentration was reduced in agreement with Tewarson et al. [61].

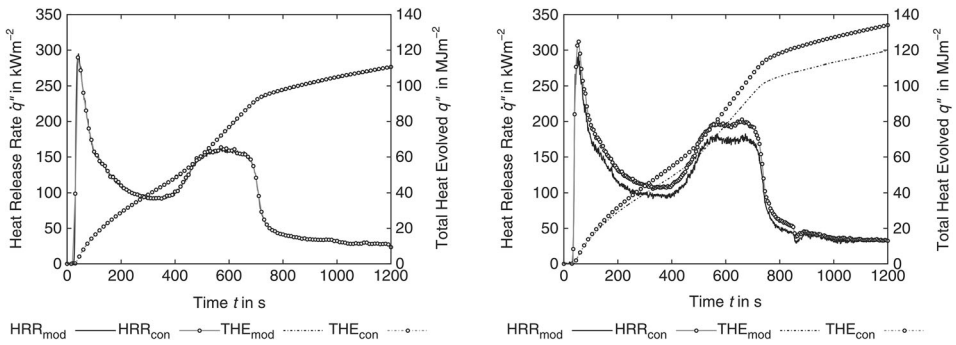

Figure 2. HRR and THE from particleboard samples at 21 vol% O_2 (left) and 18 vol% O_2 (right) displaying conventional results (subscript con) and the effect of the modified calculation procedure (subscript mod) proposed by Werrel et al. [7]. (Figure from [7]).

It should be noted that general trends may not be applicable to all fuels particularly where oxygen vitiation is thought to result in the changes to solid-phase reactions. A more nuanced understanding of burning behaviour in vitiated conditions requires the consideration of the material's chemistry and dominant reactions. This is particularly true for the materials with more complex structures or composites.

Species Yields and Production Rates—Marquis et al. [26] found that the presence of flaming combustion was a key contributor to production rates and species yields when measuring through a CACC coupled with FTIR. The production of CO_2, CO, hydrogen chloride (HCl) and hydrogen cyanide (HCN) was shown to increase significantly for PIR samples, at 50 kW/m^2, where flaming occurred (at 21 and 15 vol% O_2) but much lower values were reported when flaming did not occur at 0, 5 and 10 vol% O_2. However, some species, namely methane (CH_4), ethylene (C_2H_4) and ammonia (NH_3) demonstrated the opposite trend, where production rates and yields increased in the absence of flaming combustion. Marquis et al. [26] concluded that the presence of flaming combustion increased species 'homogeneity'. The presence of flaming prior to the sampling point is clearly critical to the collection of fire effluent species and has been described as one of the most significant factors for consideration when measuring toxic species [5].

Hshieh et al. [34] reported that CO yields typically rose in vitiated experiments but that additional factors, such as the inclusion of flame retardant treatments, could complicate the collected data as the CO yield for treated cotton was higher at 21 than at 15 vol% O_2 [34]. Researchers have also observed added complexity when assessing the effect of atmospheric vitiation due to non-linear effects on measured properties, particularly for some composite materials. For example, CO production rates of silicone elastomers were found to both increase and decrease over the transition from ambient to vitiated conditions introducing more complex trends than reported from organic-based solid samples examined in earlier work [34, 39]. Mullholand et al. [33] found that, for solid fuels, when a material approached its extinction point, the CO yield was shown to double. This was shown for fuels such as Douglas fir, PMMA, ABS, PE in the region of oxygen concentrations between 21 vol% O_2 and 14 vol% O_2. When testing PMMA and PIR foam, Christy et al. [2] found that CO yields were shown not to change significantly between 21 vol% O_2 and 18 vol% O_2 but nearly doubled between 21 vol% O_2 and 15 vol% O_2 [2]. Dowling et al. [41] concluded that, for various lining boards, O_2 concentration had limited impact on ignition times but a notable affect on production yields.

2.1.3. Chamber Atmosphere—Under-Ventilated Conditions An abridged summary of published under-ventilated research using the CACC can be seen in Table 3.

Heat Release Rate, Mass Loss Rate and Effective Heat of Combustion—Mustafa et al. [21] tested pine wood sticks at 35 kW/m^2 at an inflow rate of 9.5 L/min and compared the results to those from well-ventilated experiments using the same apparatus. The samples demonstrated a steady MLR of 0.07 g/s, for both under-ventilated and well-ventilated conditions, but a significant difference in HRR with two peaks in the HRR history, typical for charring samples, observed in the well-

Table 3
Literature Summary for Under-Ventilated Tests Using Both Open and Closed CACCs

References	Material type/thickness	Irrad. (kW/m^2)	Diluting gas and inflow rate	Extract fan flow rate
Hietaniemi et al. 1999 [31]	Nylon, PP, insecticides, herbicides, acids	25, 50	N_2/air mix Flow not reported	Not reported
Olson et al. 2005 [20]	2.4 mm clear PMMA	10, 25	Air with a flow rate of 0.67 L/s[a]	
Irshad et al. 2014 [62]	Ø20 mm pine and ash sticks	50, 70	9, 12.8, 14, 19.2, 25.6 g/(m^2 s)	24 L/s
Andrews et al. 2015 [11]	Various aircraft blankets folded	40	20 g/(m^2 s)	Not reported
Fourneau et al. 2016 [9]	n-Heptane	Not reported	20, 32, 40, 70, 100 L/min	Not reported
Irshad et al. 2019 [23]	5 100 × 20 × 20 mm rectangular pine sticks	50, 70	9, 10.2, 12.8, 19.2, 25.6 g/(m^2 s)	Not reported
Mustafa et al. 2019 [21]	5 100 × 20 × 20 mm rectangular pine sticks	35	19.2 g/cm 2 (6 to 28 L/min)	24 L/s

References	Global equivalence ratios	Type of CACC	Gas analysis type and location	Chamber dimensions and insulation	Load cell cooling and insulation
Hietaniemi et al. 1999 [31]	0.2 to 2	Chimney present, length not reported	FTIR, GC-MS within the exhaust duct	Not reported	Load cell located within chamber
Olson et al. 2005 [20]	4	ELSA[b] (closed)	CO/CO_2 analysis in exhaust system	Not reported	Load cell hung above cone
Irshad et al. 2014 [62]	1.2 to 6.8	Open with a 21 cm long chimney with an Ø8 cm	FTIR sampled from chimney exit centreline. $CO/CO_2/O_2$ analysis within exhaust duct	38 × 30 × 33 cm high chamber with a glass window for observation	No water cooling to the load cell. Load cell within chamber
Andrews et al. 2015 [11]	2 to 10	Open—unreported dimensions	FTIR with sample taken from chimney	Not reported	Not reported

Table 3 continued

References	Global equivalence ratios	Type of CACC	Gas analysis type and location	Chamber dimensions and insulation	Load cell cooling and insulation
Fourneau et al. 2016 [9]	0.4 to 3	Open—60 cm glass chimney. Restrictor limits chimney exit to Ø 60 mm	FTIR analysis performed but sampling point not reported [c]	Stainless steel chamber. Dimensions not reported	Load cell located within chamber
Irshad et al. 2019 [23]	~ 1.3 to 8 (metered) ~ 0.5 to 2.0 (emission based)	Open Ø7.5 cm chimney 21 cm high (increased to 25.8 cm due to 20 hole gas sampler). Added a 90% blockage to chimney exit	FTIR analysis used single, 4 hole with grid mixer and 20 hole gas samplers. Sample probe in between the chimney entry and cone heater	No insulation—38 × 30 × 33 cm Insulation—33 × 27.5 × 30.5 cm (l × w × h)[e]	Load cell water cooled using an insert plate. 20 mm ceramic fibreboard below sample to protect load cell
Mustafa et al. 2019 [21]	~ 0.4 to 2.0	Open—25 cm total chimney length, with an Ø8 cm. Used orifice plate at the top of the chimney	FTIR sample probe located at the chimney entrance. DMS 500 and oxygen analyser located in exhaust duct	38 × 30 × 33 cm high chamber with a glass window for observation Insulation board applied to walls and door	Load cell located within chamber. Insulation board located below sample to protect load cell

[a]Flow rates are controlled by the extract fan rate in closed systems
[b]The equivalent low stretch apparatus (ELSA) was an inverted cone calorimeter located at the NASA White Sands test facility
[c]Photos of the experimental setup suggest that the sampling point was located within the exhaust ductwork
[d]To provide a concise summary of the available literature one article has been removed from this table including (Mustafa, 2019) [24]
[e]Insulation was applied to the walls and door and was either 20 mm ceramic fibreboard (config 2) 25 mm superwool insulation (config 3)

ventilated case but a steady HRR in the under-ventilated sample. When testing various pesticides and liquid solvents, Hietaniemi et al. [31] found decreasing HRR and CO_2 yield, whereas CO, HCN and NO_2 yields increased at under-ventilated conditions. These findings were only true for chlorine-free compounds. For chlorine containing materials, it was shown that reduced burning efficiency, caused by the lowered ventilation, had a negligible effect on HRR and species yields.

Fourneau et al. [9] calculated HRRs for heptane pool fires using both oxygen consumption and carbon dioxide generation methods, and found that the results obtained from the two methods were in good agreement for the tests conducted at 100 and 70 L/min. Reasonable agreement was also reported for the case at 40 L/min, but the agreement was poor at 32 and 20 L/min with the oxygen consumption method recording 10 to 15% higher HRRs. However, earlier work on other flammable liquids suggested that disagreement between HRR calculation methods is not anticipated for all fuels as good agreement was reported for flow rates between 20 L/min and 100 L/min with consistent reduction in HRR where lower flow rates were used [63]. These results suggest that the selection of the HRR calculation method is more critical at lower flow rates but that this is not the case for all fuels. This discrepancy was reported to have been caused by the high unburned species production at under-ventilated conditions, which would not have been considered in the calculation of HRR [9]. Fourneau et al. [9] also noted that, in under-ventilated tests, the MLR does not change significantly due to a variable inflow rate as has been shown for vitiated tests [19, 53].

Species Yields and Production Rates—Fourneau et al. [9] described a significant increase of CO yield from ~ 0.001 g/g to ~ 0.22 g/g when the chamber inflow rate was reduced. However, inflow rates had a much smaller effect on unburnt hydrocarbon species yields and were shown to only increase slightly. Mustafa et al. reported a greater generation of ultra-fine particles using a CACC coupled with a DMS500 than had previously been reported in literature [21]. When using the Lethal Concentration 50(%) (LC_{50}) methodology they reported that the initial toxicity (and peak toxicity) was greater for well-ventilated tests prior to sample ignition but for the majority of the tests (after well-ventilated sample ignition at approximately 192 s) under-ventilated tests had higher LC_{50} [21]. DMS500 results saw the higher particle concentrations at peak HRR outputs for both well- and under-ventilated cases. Under-ventilated tests had a higher generation of total particles as well as ultra-fine particles [21].

2.2. Open-CACC Design Features

Prior to discussion of open-CACC features, it is useful to highlight the work of Austin et al. [64, 65] on the gasification apparatus. The design intent of the experimental rig used in the aforementioned work is similar to the CACC as an imposed irradiance is applied under conditions where the localised oxygen concentration is controlled. The complexity of this apparatus highlights some of the challenges faced where accurate control of experimental atmosphere is desired. The apparatus features a sealed cylindrical chamber where a controlled gas mixture is introduced at the bottom of the chamber through gas inlets. The gas inlets are

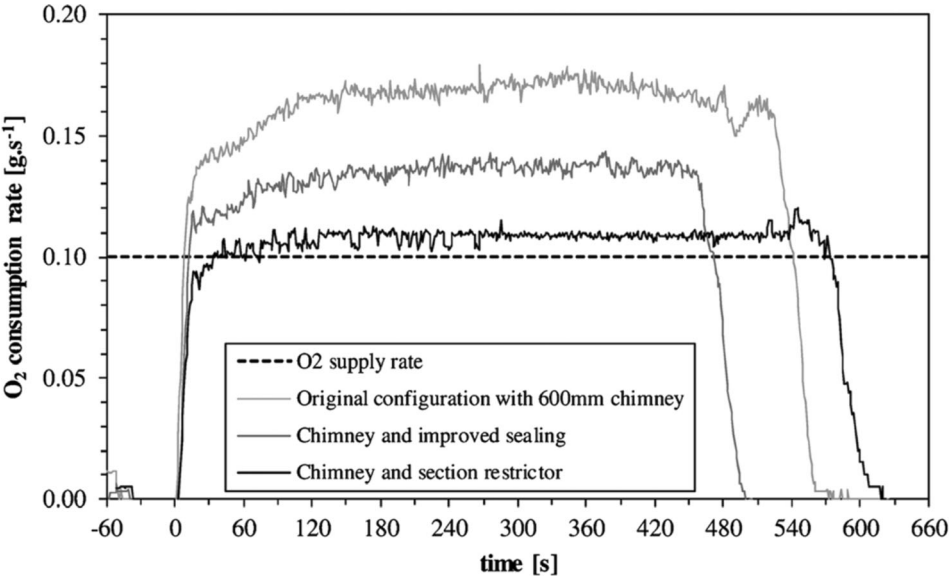

Figure 3. PCO effect recording overconsumption of O_2 during acetone pool experiments with various mitigation measures taken. (Figure from [9]).

located beneath layers of glass beads to improve atmospheric uniformity within the cylinder. The cone heater is larger than that of a CC (using three rather than one coiled element) to improve heat flux distribution over the sample surface. To vary the imposed irradiance, the sample's distance from the cone heater is varied rather than the cone temperature so as to maintain the spectral distribution of the heat flux. The internal walls of the chamber are painted black and are water cooled to 25°C to reduce re-radiation imposed onto the sample. The sample holder consists of a borosilicate glass dish insulated by 5 cm Foamglas® insulation with thermocouples located at various heights in the centre of the dish and gas sampling taken immediately above the sample surface. Windows and mirrors into the cylinder allow observation of the sample during the test. The design features of the gasification apparatus offer an insight into the added complexity necessary to achieve satisfactory atmospheric control. It is clear that any attempt to experimentally produce a non/partially oxidised environment requires a sophisticated approach. From the context provided by the gasification apparatus, the following section will discuss research into some open-CACC features and the sensitivity of experimental outputs to the variation of these features.

2.2.1. CACC Chimney The earliest reported CACC designs had no separation between the combustion chamber and the exhaust hood. These designs, typically referred to as closed-CACCs [7], did not require a chimney [3]. However, due to practical considerations such as safety, adaptability and costs, research featuring CACCs with no direct connection between the combustion chamber and the

exhaust duct has become more common [19]. The open-CACC, first reported in [45], has the undesirable consequence of allowing interaction between the combustion gases and the surrounding atmosphere causing post-chamber oxidation (PCO) during effluent transition from the CACC chamber to the extract duct. PCO can cause over-consumption of O_2 in the exhaust duct gas analysis resulting in inaccurate measurements. The extent of O_2 overconsumption, and some mitigation methods, are shown in Figure 3. Marquis et al. identified the need for ISO TC 92 to develop a chimney that reduced PCO and noted the use of a quartz chimney would also allow visibility of any flaming within the chimney [46] which can result in modified conditions within the chimney when compared to the CACC chamber [53, 54]. Marquis et al. [26] remarked that any flaming above the chimney would invalidate FTIR analysis and therefore only materials of ''low calorific potential'' could be tested. This was found to be particularly true at higher heat fluxes where the fire effluent is likely to be more reactive as it exits the chimney [54]. Any flaming attributed to the apparatus design, rather than the conditions applied to the sample surface, may present misleading toxic properties necessitating in the use of a CACC chimney to reduce the likelihood of PCO by allowing the cooling of effluent prior to atmospheric mixing. Chimneys used in open-CACC designs, as described in Table 2, are usually in the region of 20 to 60 cm, although up to $\sim$ 1 m has been reported in [66]. It has been reported that longer chimney lengths show better agreement with large-scale data [6, 66] although no detailed study has compared various chimney lengths to refine this general statement.

Post-chamber Oxidation and Toxicity Measurements—PCO has raised concerns over toxicity data collected using the open-CACC [67] with resulting diluted species considered non-representative of post-flashover fires [66]. However, other authors have noted that many methods used for similar data collection also introduce entrained air to avoid water condensation disrupting the toxic species collected [23]. They argued that by collecting ''raw'' samples directly from the CACC chimney, rather than from the exhaust duct, and carrying the effluent via heated lines, dilution of effluent by entrained air can be prevented. Andrews et al. noted that collection of species within the CACC chimney has the advantage of preventing dilution of effluent in air, which would otherwise risk reducing concentrations of certain toxic species below measuring device detection limits [11]. Additionally, the collected species from the CACC chimney allow the use of a continual heated line to the analyser preventing thermal cooling, which would result in losses of condensable gases were the sampling point to be located at the exhaust duct [24]. However, there are some reported advantages to locating the sampling point within the exhaust duct as it allows more meaningful comparisons between toxic species and smoke measurement due to the proximity of sampling point and the laser extraction beam [24]. This advantage allowed Mustafa et al. [24] to report no correlation between smoke production and increased production rates of particles smaller than 50 nm, indicating that these hazardous particles were not identified by typical assessments of smoke production.

Some have justified the use of species sampling within the exhaust duct by arguing that PCO is not anticipated. For example, Mustafa et al. [24], when conducting tests on pine stick samples at 9.5 L/min air inflow rates at 35 kW/m^2,

reasoned that due to the low temperatures within their chamber (below 600°C) PCO of the carbonaceous particles was not anticipated and therefore particle collection from the exhaust duct using a DMS500 particle analyser was reasonable. However, research into synthetic polymers has typically required the relocation of sampling points in order to collect meaningful data unaffected by PCO with some typical sampling locations highlighted in Figure 1. An ISO 13927 [68] metal chimney was used by Marquis et al. [47] who reported that that the ring probe used was suitably downstream to allow for adequate mixing although no evidence is given to support this. Marquis et al. [26] also noted that the chimney must be sufficiently long so as to obtain uniform mixing within it. The authors used a 0.6 m long chimney in their work although other authors have used a CACC coupled with FTIR with a smaller chimney [11, 62]. There has been no investigation into the sensitivity of gas analysis to different chimney lengths to validate the claim of uniform mixing in the CACC chimney in [26] or [47]. Gomez et al. [51] reported HCl yields for PVC that were close to the theoretical yield despite using a CACC with no chimney and a FTIR sampling point located at the exhaust duct. In cases where the sum total HCl yield was below its calculated theoretical value it was reasoned that the losses may be due to soot particle deposition along the walls of the chamber and exhaust duct [51].

The different methods of oxygen depletion, vitiation and under-ventilation, introduce challenges for the gas analysis coupled at the CACC chimney. In under-ventilated tests there is the potential for a counter-flow of ambient air to enter into the chimney and diffuse with the fire effluent at the ring probe [26]. Whilst high air/N_2 inflow rates mean this is less likely for vitiated tests, the assumption that the pressure inside the chimney remains ambient, which is used to calculate species generation rates, is less likely to be true and subsequently introduces added calculation uncertainty [26]. Mustafa et al. [21] reported that the inclusion of the 3 L/min FTIR sample flow taken from the chimney had the unwanted consequence of drawing more air into the chamber from the chimney opening [21] as it was significant relative to the inflow rates for under-ventilated tests [24]. Irshad et al. [23] identified a lack of effluent mixing within their 250 mm chimney, and in particular, entrainment of surrounding air into the sampling point located at the top of the chimney. After further investigation Irshad et al. [23] concluded that using a 20 hole mean gas sampler at the base of the chimney in combination with the grid plate restrictor at the top of the chimney was the most effective method of reducing air entrainment. Knez et al. [25] conducted tests on wood samples with gas sampled at the top of a 500 mm chimney using glass wool filters and did not report any of the concerns raised by Mustafa et al. [21] regarding air entrainment into the chimney. This was possibly due to the greater chimney length as well as the significantly greater chamber inflow rate used by Knez et al. [25] (144 L/min) resulting in a negligible impact from the gas sampling flow also used by [25] (4.32 L/min) when compared to the difference in chamber flow and gas sampling flow used in [21] (6 and 28 to 3 L/min). Chatenet et al. [22] located an FTIR probe and a cascade impactor (an ELPI Analyser) at the top of a 600 mm chimney resulting in a 150 mm extension of the chimney. Oxygen concentration (21 to 2 vol% O_2) was reported to have no effect on fire effluent gas production or particle

sizes/size distribution. Chatenet et al. [22] did not report any concerns with air entrainment at the top of the chimney in this instance and further work is necessary to determine the value of a plate restrictor when sampling from the CACC chimney.

Research on compartment fires has indicated that where effluent temperatures drop below approximately 800–900 K, CO oxidation to CO_2 is "frozen out", with chemical reactions quenched at lower temperatures [69, 70]. In order to ensure oxidation reactions do not continue beyond the CACC chimney the effluent leaving the chimney must be at a sufficiently low temperature. This is partly influenced by the chimney width and length but also by the thermal losses from the chimney, the applied irradiance from the cone heater, the heat released from the sample and the position of the sample within the enclosure. There has been no reported study of the temperatures of fire effluent leaving the CACC chimney at various operating conditions to the best knowledge of the authors.

The use of a chamber, and chimney, in the CACC introduces concerns that had previously been raised for the smoke density chamber regarding the deposition of species along the apparatus surfaces leading to the gas sampling point [5]. There is considerable uncertainty regarding the losses that result from surface deposition, and the impact of surface material, particularly for acid gases such as HCl that are considered vulnerable to this effect [71]. Repositioning gas sampling to within the chimney has the advantage of reducing the impact of wall deposition within the extract duct as well as reducing post chimney dilution of toxic species. However, the chamber may increase the absorption of toxic gases with combustion generated aerosols where they build up within the combustion chamber resulting in the trapping of species on sampling filters [71]. These effects have been attributed as some primary reasons for the lack of consistent data on HCl and other acid gases [71], and perhaps their subsequent underestimation as important toxic contributors, and further research is required to determine the measures necessary to optimise gas sampling. Despite its effect on toxicant deposition, none of the reviewed literature gave a detailed account of chimney cleaning procedure or its frequency within the experimental methodology. Further to this, the effect of neglecting to perform chimney cleaning was rarely discussed within data analysis. As ISO/TS 5660-5 does not currently provide guidance on chimney cleaning procedure, further research is needed to determine the effect of toxicant deposition on metal surfaces where detailed emission measurements are made.

Post-chamber Oxidation and HRR—Marquis et al. found that to achieve the two primary aims of the chimney, i.e., preventing ambient air backflow and flaming outside of the combustion zone, a 60 cm chimney was sufficient for tests using PMMA at 50 kW/m^2 for oxygen concentrations ranging from 10 vol% to 21 vol% [19]. After comparing the experimental results with and without a 60 cm metal or quartz chimney, and with a cone calorimeter, Marquis et al. [19] concluded that the accuracy and repeatability of the apparatus was not affected by the inclusion of a chimney at 21 vol% O_2 and that results were similar between the designs. However, this was not shown to be true for vitiated conditions, as illustrated in Figure 4, where the CACC without a chimney was shown to overpredict peak HRR (PHRR) for 12 to 15 vol% O_2 and underpredict PHRR for 10

vol% O_2. The contradictory effect that a CACC without a chimney had on PHRR at various oxygen concentrations was thought to be due to an increased entrainment of surrounding air. At 10 vol% O_2 this resulted in the dilution of combustion gases such that they fell below the flammable limit for the mixture thereby preventing flaming and underpredicting HRR. Marquis et al. [19] concluded that a CACC without a chimney was unsuitable to examine gas phase phenomena in vitiated conditions but, since MLRs were shown to be unaffected by the use of a chimney in vitiated conditions, solid phase phenomena could still be studied. Regarding the material used for the chimney itself, quartz or metal, Marquis et al. described the differences as having "significant effect on physical and chemical processes" [19]; although it should be noted that, for the data provided on HRR and MLR measurements, the changes appear to have negligible effect on the experimental results for PMMA. The effect of chimney type and length has only been reported for PMMA and further examination of other materials is necessary to increase design confidence for a range of material types.

Marquis et al. [47] reported that, at 15 vol% O_2, flaming combustion occurred within the CACC chimney rather than on the sample surface. The separation of flames from the sample surface in vitiated conditions reduced thermal feedback to the sample and therefore changed the relationship often observed between HRR and MLR. For the test at 15 vol% O_2, a rise in the HRR occurs without a corresponding increase in the MLR [47]. A similar case was reported for 3 mm ABS samples [53, 54], 14 mm PMMA [49] and 30 mm PIR rigid samples [26] where flaming within the chimney was observed at an irradiance of 50 kW/m^2 and for oxygen concentrations of 12.5, 10, and 15 vol%, respectively. The authors concluded that where flaming combustion does not occur, i.e., < 15 vol% O_2 for [26], 47], < 10 vol% O_2 in [49] and < 12.5 vol% O_2 for [53], condensed-phase degradation remains consistent, irrespective of further reduction in oxygen concentration, because there is no radiation from the gas phase whilst the cone irradiation remains the same. Marquis et al. proposed that this is caused by the apparatus design and is the result of strain effects causing premixed flaming due to turbulence within the chimney [26].

Linnå and Wahlström [72], as described in [17], tested 10 mm particleboard and found the CACC without a chimney overpredicted the HRR by at least $\sim 20\%$ due to PCO. Werrel et al. [7] attempted to mathematically compensate for the implications of an open-CACC chimney when calculating HRR. The researchers intended to quantify the errors that dilution effects from the two partial flows into the exhaust hood introduced to the existing HRR calculations [58]. This was mitigated by introducing changes to the conventional baseline approach used in the CC (where an initial 60 s reading prior to testing took the average oxygen mole fraction to obtain a constant baseline) so that an instantaneous oxygen baseline was calculated using the oxygen mole fraction within the chamber (averaged over 60 s prior to the test) and the change in duct mass flow during the test. The altered baseline approach was then used to modify HRR calculations.

When Werrel et al. compared results using both calculation methods it was evident that the conventional calculation method overpredicted HRR. The magnitude of the overprediction increased as the oxygen concentration within the

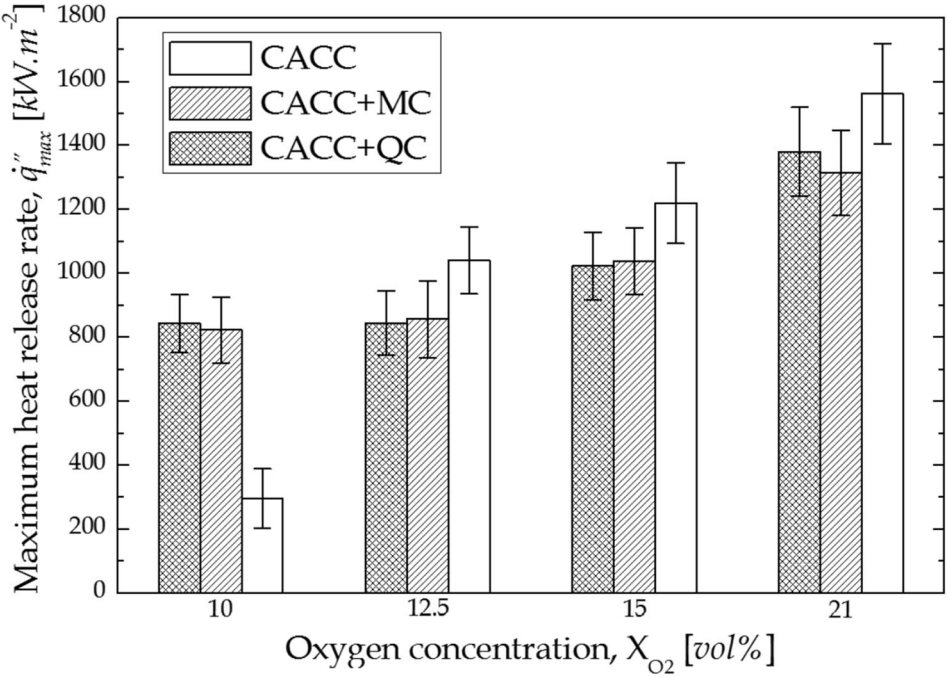

Figure 4. Influence of open-CACC design on peak heat release rate (Figure from [19]) (*MC* metal chimney, *QC* quartz chimney).

chamber was reduced, with results showing minimal differences between calculation methods at 21 vol% O_2 but 30% overprediction at 15 vol% O_2. Werrel et al. [7] reported that the overprediction of HRR is due to the error in the constant oxygen baseline value being equated to oxygen consumption within the conventional calculation method. Their work concluded that some of the physical aspects of dilution caused by the open connection had been addressed, but other factors, such as the physical implications of cooling and mixing as well as chemical interactions between the fire effluent and the surrounding air, had not [7]. Werrel's corrected equations for CO and CO_2 mass flow were used by Barton et al. [29] when reporting CO and CO_2 yield data for ambient and vitiated tests with electric cables and a mineral oil. Comparisons between the corrected and uncorrected yield data showed that they were only marginally altered between calculation methods.

2.2.2. CACC Combustion Chamber The CACC has been described as being "highly dependent on mixing conditions" [54] with the shape of the combustion chamber, as well as the chimney extension and flows through the control volume, influencing the imposed atmospheric conditions. Chamber dimensions for open and closed CACCs are given in Tables 1, 2 and 3, showing that similar dimensions are typically used, particularly for recent open-CACC designs. A number of

CACC designs have reported some difficulties achieving an appropriate degree of airtightness [9, 26, 54]. Marquis et al. [26] could not create a 0 vol% O_2 environment within their tests and identified the CACC door as the primary cause of leakages. To improve airtightness, they used a foam seal between the door and the chamber as well as aluminium duct tape on the door junction to the chamber to achieve an oxygen concentration of 0.1 and 0.7 vol%. Fourneau et al. [9] also reported problems with chamber airtightness and replaced a number of seals to improve results. The failure to create 0 vol% O_2 atmospheric conditions may limit conclusions on whether the measured O_2 was the result of an inability to create inert conditions or a by-product of the combustion taking place within the chamber. However, ''significant changes'' [26] would be the only solution to improve the airtightness of the CACC.

Preheating of the sample, caused by reradiated heat from the chamber walls and shutter, has been a concern throughout the development of the CACC. Early designs by Babrauskas [3], as used in the work of Mullholand et al. [33], used a water-cooled shutter to minimise pre-heating after sample insertion whilst atmospheric conditions stabilised. The chamber walls in [3] were primarily pyrex panels with the desire to minimise heat build-up within the chamber as well as allow visibility during the experiments. Despite this, the designers acknowledged that heat build-up would indeed be anticipated, and that pre-heating time should be kept to a minimum. Chamber wall re-radiation has been mitigated using other methods. For example, Christy et al. [2] cooled the CACC chamber using walls made of two layers of stainless steel, painted black, with water channels running between them. This design also featured a unique method for reducing sample pre-heating during atmospheric stabilisation involving an electronically operated arm in place of a shutter that rotated the sample away from the cone heater until conditions were satisfactory for the commencement of testing [2]. The precursor to the standardised apparatus [10] features a chamber cooling method first reported by Mikkola [45] where water cooling of the junction between the cone heater and CACC chamber was used to prevent overheating of the chamber walls with similar approaches being utilised elsewhere [2, 19, 29, 53]. Marquis et al. [26] identified that, by the time the CACC test starts, there was already a temperature gradient within 30 mm PIR samples measured using thermocouples at 6, 15, 24 and 30 mm from the sample's surface caused by preheating inside the CACC chamber. As a large extent of sample pre-heating from the cone heater and chamber walls occurred during the 60 s O_2 baseline collection, the experimental methodology as described in Marquis et al. [19] has since been adapted in ISO/TS 5660-5 [10] to feature the O_2 baseline collection prior to the insertion of the sample as used by Werrel et al. [7].

Gomez et al. [50] compared CACC and CC repeatability using results from a CC round robin study and found that ignition times, peak HRR, average HRR and smoke production rates fell within the acceptable range for various materials (including PVC, PIR foam and plywood). They subsequently concluded that, at the tested flow rates of 150 and 180 L/min, the CACC provided results with statistically insignificant differences up to an applied irradiance of 75 kW/m^2 and therefore the effect of enclosure preheating was negligible [50]. However, a high

CACC chamber temperature was reported by Blomqvist et al. [13, 32] to cause the load cell reading to drift upwards and that this was particularly an issue for materials with a low mass coupled with a low MLR. Load cell drift was also a concern for Beji et al. [18] when using a closed-CACC. In their case a gypsum board was installed above the load cell and a number of cooling channels were installed around the load cell stem. The coverage of the gypsum board protection was so extensive that three rectangular vents (each 50 mm by 100 mm) were necessary to achieve adequate flow mixing throughout the chamber. These features, along with 18 and 57 mm thick calcium silicate walls around the side and bottom of the sample holder respectively, adequately reduced heat losses and prevented load cell malfunction at 25 and 50 kW/m^2 irradiance [18]. Well-mixed conditions were reported, inferred from uniform conditions measured within the chamber, despite the gypsum board obstruction. However, accumulation of unburnt fuel vapour within the chamber, leading potentially to backdraft conditions, were reported due to the high molecular weights of the fuels compared to air [18] although the gypsum board obstruction may also have contributed to this.

Reducing Chamber Heat Losses for Toxic Species Collection—As previously noted, the chamber walls in many CACCs have been designed to prevent heat build-up within the chamber. There are several reasons why this is preferable for testing conditions. Firstly, should heat be retained within the chamber, reradiation of heated chamber walls onto the sample would be expected. Reradiation may reduce the uniformity of spectral irradiance imposed onto the surface of the sample, a key measure for ensuring repeatability and reproducibility, and no research into the impact of insulated CACC walls has quantified this effect. Secondly, the use of insulation would also limit comparisons between the CACC and CC as well as limit the use of the CACC for experimental work replicating well-ventilated flaming conditions. PCO is also considered more likely at higher heat fluxes [54] and therefore this unwanted effect would occur more frequently when heat losses are reduced, which in turn can cause the overheating and more frequent malfunction of the load cell as reported in [11, 24, 62].

Despite this, there is a desire to reduce heat losses in order to better simulate post-flashover fire conditions, because heat losses have been identified as the cause of underpredicted CO and HCN yields when compared to under-ventilated fires at larger scales [66]. In some vitiated tests, only intermittent flaming, with no prolonged steady-state flaming period, was found when oxygen concentrations were reduced creating unpredictable results for species yields [32]. Stec [5] argued that this is because the heat flux applied to samples is insufficient to replicate post-flashover fires and therefore sustained flaming does not occur in the CACC where it would do so at similarly reduced oxygen concentrations in large-scale enclosure fires. As sustained flaming has been shown to be of critical importance to species yields it is necessary to induce flaming at reduced oxygen concentrations in order to replicate and reproduce post-flashover conditions within the CACC. This was reiterated by Knez et al. [25] who explained that species yields are controlled by both oxygen availability and gas temperature but only one of these can be defined by the user without either thermal insulation or a temperature control system included in the CACC design. This effect has been attributed as the specific cause

of species rate underprediction with Fourneau et al. [9] concluding that collected species yields are often reported to be much higher in under-ventilated tests than in vitiated tests due to the premature onset of extinction where, in vitiated tests, the mass flow rate of oxygen still satisfies $\phi < 1$ when extinction occurs.

Irshad et al. [23] attempted to achieve adiabatic conditions within the CACC chamber believing that, due to the heat losses from the CACC, the conditions were not representative of a compartment fire. A combination of cooling using a water cooled insert plate and 20 mm ceramic fibre insulating board was used to prevent heat losses through the load cell in [23] where it was reported that load cell malfunction was a consistent problem at 70 kW/m^2 but less so at 50 kW/m^2. To prevent heat losses, Mustafa et al. [21] fitted an insulation board to the internal walls of the chamber and insulation over the observation panel that could be temporarily removed to inspect the sample during the test. This insulation, made of 25 mm superwool insulation board by Irshad et al. [23], reduced the volume of the enclosure and was reported to increased MLRs, production of CO, total hydrocarbon (THC) and chamber equivalence ratios, as illustrated in Figure 5, as well as increase temperatures measured 5 mm above the sample surface by 50°C.

2.2.3. CACC Irradiance The CACC cone heater, spark ignitor, and sample holder have all been retained from the original CC design. It is therefore anticipated that the effective heat flux coverage over the exposed sample, reported to be 97.25% at 30 kW/m^2 at a 2.5 cm distance between the holder and cone heater [73], remains unchanged unless altered by significant reradiation from the chamber walls. General trends, such as an increased repeatability for high heat fluxes [74], are also expected to remain true. Interestingly, however, a reduced CACC repeatability was shown for PMMA at 50 kW/m^2 when compared to 20 and 35 kW/m^2 [19]. Marquis et al. [19] suggested that this was due to high reaction speeds in the gas phase leading to a high mass flow cooling of the steel container of the CACC and the subsequent reduction of reradiation from the chamber walls. However, this hypothesis was purely speculative with no quantifiable analysis included within the study and is worthy of further research to better understand this observation. As with the CC the regression rate of fuel alters the view factor on the sample surface thereby changing the imposed heat flux. This regression has led to differences of 5 and 30% between the intended irradiance setting and the average radiative heat flux received by the sample [18]. Note that this is not a limitation exclusive to the CACC. However, one of the solutions proposed by Beji et al. [18], the addition of a fuel supply line to maintain the fuel surface flush with the top of the sample holder, becomes more challenging due to the CACC enclosure and the need to reduce leakage points into the chamber.

Reservations that exist for the CC regarding the choice of imposed irradiance, and their relevance to each fire stage, remain for the CACC. Mun et al. [55] suggested that more research should be done to ensure that the selected heat fluxes imposed on samples are representative of compartment fire conditions as this choice affects the CO yield and soot production data collected that is in turn used in fire risk analysis. Discussions from ISO TC 92 in 2015, as reported in [66], highlighted that the CACC would only be suitable up to irradiance levels of

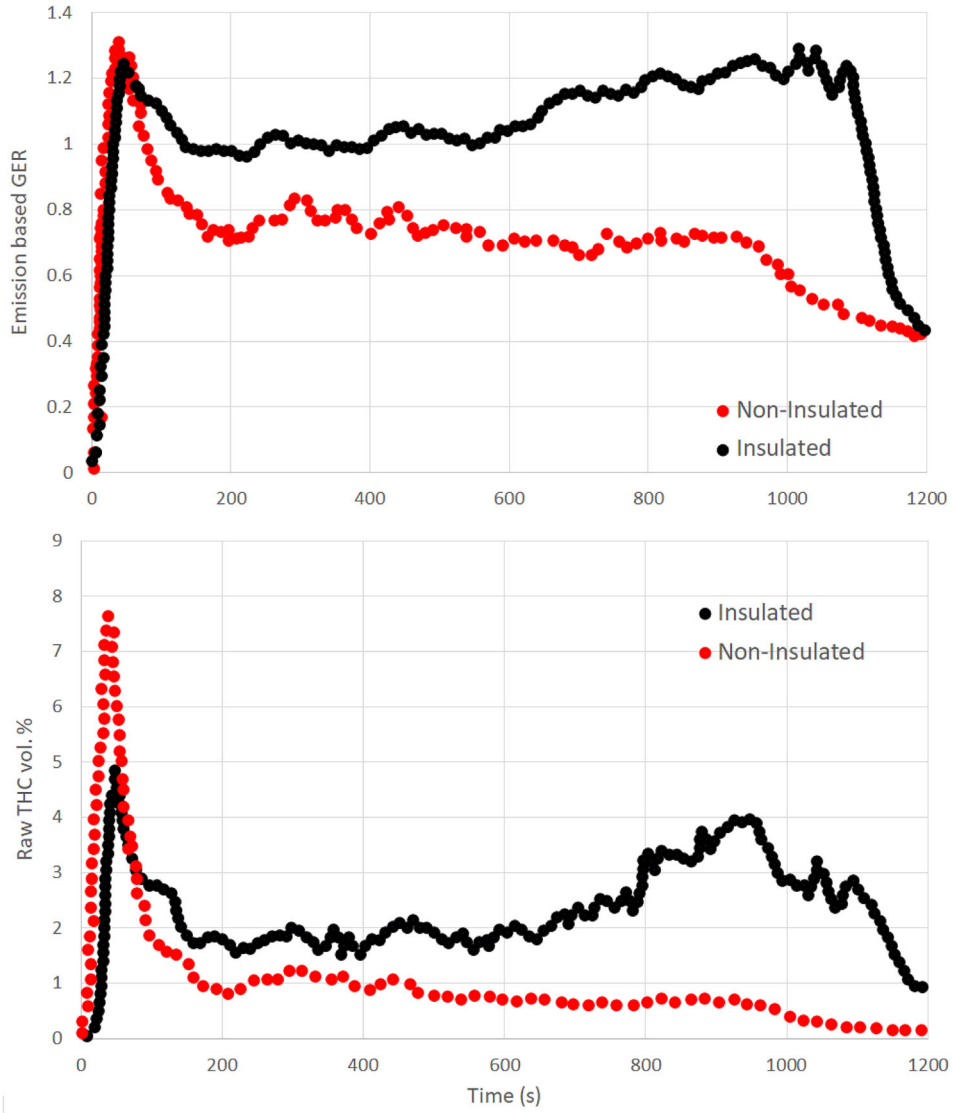

Figure 5. CACC with and without the provision of 25 mm of superwool insulation to the internal walls for GER and THC for pine sticks at 50 kW/m² respectively (Figure recreated from [23]).

50 kW/m^2 for many materials due to the delay caused by atmospheric stabilisation leading to an early decomposition of samples above this irradiance level. Blomqvist et al. [13] reported that some 50 mm polymeric foams melted during the 90 to 120 s imposed to reintroduce atmospheric stability despite the shutter insulating the samples from 50 kW/m^2 irradiance. They also highlighted large peaks in CO concentration at the start of tests within the CACC as an indication

of this preheating effect. This was considered particularly misleading (leading to yield under-prediction) when attempting to collect yield data from non-combustible materials where the initial interaction of the sample with the heat source was critical to the overall toxic yield output collected [13, 32]. However, limiting cone irradiance of the CACC to 50 kW/m^2 is of particular concern because one of the primary challenges when attempting to replicate large-scale fires is its perceived inability to adequately characterise CO and HCN yields below 10 vol% O_2. This is in part because the energy applied to the sample by the cone heater is inadequate compared to larger-scale conditions [66] where, it is said, oxygen concentrations as low as 5 vol% O_2 may still facilitate combustion due to the intensity of the radiative heat applied by the smoke layer [5].

2.2.4. CACC Diluting Gas Inflow Rate Many early, closed-CACC designs included numerous features for dissipating the flow field before reaching the flaming sample including baffle plates above each inlet pipe, a wire mesh screen and a layer of glass beads [3]. Glass beads and aluminium plates were similarly used to dilute the inflow of N_2/air mixture by Leonard et al. [35] whose design also featured a plenum prior to the CACC chamber. These features were said to make the inflow "noticeably less turbulent" [35]. In standardised open-CACCs baffle plates located above two gas ports are used with the inflow rate typically controlled by rotameters. Mixing inside the chamber is monitored using an oxygen analyser connected to the gas inflow and a second oxygen analyser connected to the combustion chamber itself [19, 49]. Whilst the CC flow field surrounding the sample is not well characterised it is generally accepted that it is well stabilised directly above the surface of the sample [20, 36]. There has been no research to ensure that this remains true for the CACC. The inflow rate has been described as one of the most important parameters in CACC tests [48] for controlling conditions within the CACC chamber [49]. Some have criticised the CACC because it does not adequately quantify all of the oxygen present in the incoming gases that bypass the flaming region [5], arguing that this unknown leaves the ventilation condition undefined when compared to other apparatus such as the SSTF.

Using a closed-CACC Petrella tested PS and PMMA at flow rates ranging from 9 L/s to 24 L/s and reported that peak HRR was only marginally affected by changes in flow rate and changes to TTI were negligible [38]. Marquis et al. [49] conducted tests on black PMMA at varied flow rates of 100 ± 5 130 ± 7, 160 ± 5, and 190 ± 7 L/min, at 50 kW/m^2 irradiance and 21, 15 and 10 vol% O_2. The results showed that CO production was higher, and HRR lower, for lower flow rates for both ambient and vitiated tests. Flow rates 160 and 190 L/min produced similar HRR and CO production although at 10 vol% O_2 the comparison between flow rates is not as clear due to observed differences in TTI as shown in Figure 6. The TTI at 10 vol% O_2 was shown to be significantly affected by the inflow rate with greater delays to ignition at higher inflow rates but this was not true for other oxygen concentrations tested. Marquis et al. [49] concluded that, when the flow rate was too low, the gases within the chamber were not suitably replaced with the incoming N_2/air mix, leading to an accumulation of gases creating under-ventilation in the chamber, and that this impacted the gases collected

within the hood such that the accuracy of measurements was reduced. A flow rate of 160 L/min was found to keep the CO/CO_2 ratio below 0.05 g/g and thus avoid under-ventilation of the CACC chamber [49]. Marquis et al. concluded that it was important to maintain the flow rates suitably high so as to avoid the build-up of fire effluent within the CACC chamber, which could increase the likelihood of fire effluent oxidation during the tests [49]. None of the inflow rates tested by Marquis et al. [49] were shown to affect the condensed phase decomposition as the MLR remained consistent between tests. Because of this it was concluded that the flow rate into the chamber did not have a cooling effect on the surface of the sample or lead to a reduction in flame temperature. Marquis et al. [49] noted other risks, should the inflow rate be too high, such as the introduction of localised turbulence leading to unrealistic mixing in the gas stream or increased velocity inducing a jump in reaction rate in the condensed phase. Marquis et al. [49] found that a flow rate of 160 L/min was favourable for avoiding under-ventilation without inducing greater turbulence to the gas phase. However, as results were only reported for PMMA, there is a need for a wider range of materials to be examined.

Irshad et al. [62], compared the HRR calculated using the "raw data" collected from the fire effluent prior to leaving the CACC chimney and that collected from the extract duct. HRR data was subsequently categorised as "primary" (i.e., combustion within the CACC chamber) or "secondary" (i.e., fire effluent mixing with air after leaving the CACC chimney). The results for pine wood sticks under 50 kW/m^2 irradiance appear to show that for lower flow rates, "secondary" HRR is dominant making up 60 to 80% of the total HRR during the main period of burning. For tests where flow rates were increased "primary" HRR became dominant at $\sim 60\%$ of the total HRR output. The results indicate that inflow rate effects the proportion of HRR contribution from PCO. However, it should be noted that the tests were conducted using a 20 cm chimney, rather than the standardised 60 cm chimney, no repeat tests were conducted, and it was not reported whether flaming was observed above the chimney [62].

3. Comparisons with Other Experimental Methods and Scales

The composition and yields of fire effluents in the CACC have been found to be broadly similar to other bench-scale test methods but only when combustion conditions were comparable [13]. However, as noted by Blomqvist et al. [13], creating stable and well defined combustion conditions have proven to be a challenge. In fact, creating fire toxicity data that is scalable is reliant on clear definitions on what combustion condition the test method intends to replicate. This in itself requires the determination of ventilation conditions, specimen and gas temperatures, and flaming or non-flaming combustion [32, 75]. Secondary factors such as dilution of fire effluents with fresh air, the evolution of soot particles through space and time and the presence of unique material combinations can also have a significant impact on conditions within real fires and become difficult to replicate in a bench scale test [32]. High variability, even for homogeneous materials, often

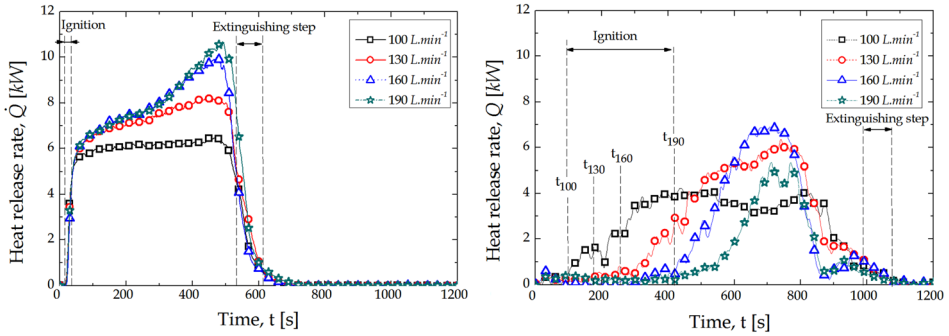

Figure 6. The effect of inflow rate on HRR for 21 and 10 vol% O_2 (Figure from [49]).

leads to conflicting data between different experimental methods, which has been said to prevent market stability and the assurance of fire safety [30]. This complexity has led to a lack of the reported data for composite, multi-component materials in their end-use form [29]. The interaction between different material types contributes to the challenge of interpreting data collected from all bench-scale apparatus and is not a challenge that is unique to the CACC. Gann et al. [30] suggested that to have confidence in a bench-scale method of collecting toxic yields, the method must be shown to perform well for a diverse range of materials and have the sensitivity of control variables settings assessed. As many end-use objects are of greater complexity than homogeneous samples there is a desire to assess samples that are more reflective of typical fuel packages [30].

The CACC has been criticised for being unable to measure toxic yields (particularly CO and HCN) for under-ventilated conditions where data is compared between the CACC and other experimental scales (for example the ISO 9705 room fire test [76]). Stec [5] concluded that only the fire propagation apparatus (FPA) and SSTF were capable of determining the relationship between equivalence ratio and toxic yields. A comparison of different experimental methods used in Stec's study [5] is shown in Figure 7. A report into potential test methods for the classification of construction product toxicity concluded that a "*significant body of work*" was necessary before the CACC could reproduce toxicity yields found in larger scales at equivalence ratios above one [66]. Hull et al. [67] concluded that the CACC typically shows lower CO yields in under-ventilated conditions and sometimes higher CO yields in well-ventilated conditions when compared to large-scale TOXFIRE data [77]. Similarly, the CACC overpredicted the CO yield of PMMA in well-ventilated conditions [13] when compared to SSTF data in similar conditions. Following this, Blomqvist et al. [32] reported a general insensitivity of CACC toxic yield data in vitiated tests to changes in the GER concluding that the SSTF offers the best means of controlling equivalence ratio. However, it should be noted that many comparisons between the CACC and other methods took place prior to the standardisation of the CACC and do not feature many of the adaptations intended to improve the value of toxicity

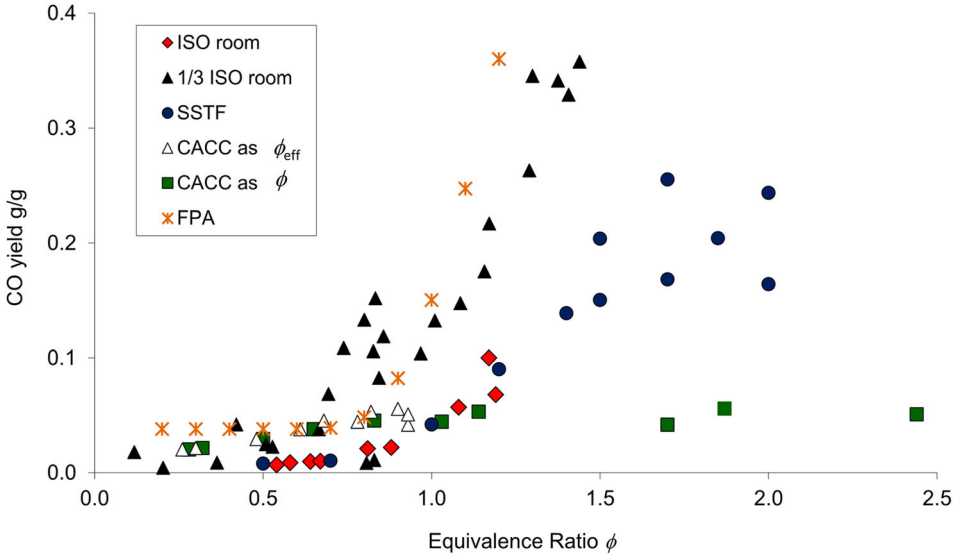

Figure 7. Comparison of CO yields from polyamide 6.6 at different ϕ (Figure from [5]).

data that is collected [5, 13, 32, 66]. There has been no thorough investigation into how CACC control variables can be adjusted to improve toxic yield scalability. There is a general need to provide updated comparisons to large-scale data using standardised apparatus featuring adaptions best suited to the collection of toxic species (such as added insulation to prevent heat losses and sampling of gases from the CACC chimney rather than the exhaust duct).

Gann et al. [30] compared a closed-CACC, SSTF, NFPA 269 radiant apparatus [78] and an ISO 5659-2 smoke density chamber [79] to room scale fires with test conditions described in Table 1. It was shown in [30] that the closed-CACC could achieve good agreement for CO_2 yields for all three materials when compared to the post-flashover conditions in the room fire tests and were within a factor of two when compared to pre-flashover conditions in the room fire tests. Interestingly, perhaps in conflict with conclusions reached by Stec [5] and Blomqvist [32], the SSTF reported very low CO_2 yields for post-flashover conditions and overpredicted pre-flashover CO_2 yields. It should be noted however that Gann et al. [30] described their use of the SSTF as an "*exploration*" because the SSTF is designed for the testing of homogenous materials only [28]. When comparing CO yields, Gann et al. [30] concluded that a conservative yield of 0.2 g/g should be used for toxic hazard calculations because none of the four apparatus were shown to consistently replicate post-flashover CO yields. The closed-CACC was again shown to overpredict CO yields in pre-flashover conditions and underpredict in post-flashover conditions. However, the closed-CACC did produce pre-flashover CO yields within a factor of two from the sofa and bookcase samples. Gann et al. [30] concluded that a closed-CACC operating at 50 kW/m^2 with oxygen concentrations

between 16 vol% and 18 vol% was the preferred bench-scale method for collecting toxic yields from under-ventilated fires. It was also concluded that a closed-CACC operating at 21 vol% O_2 was the preferred method of collecting toxic yield data for well-ventilated fires.

It is uncertain whether data collected using a CACC featuring a chamber atmosphere of 21 vol% O_2 can be directly compared to CC data. Although such attempts were made in [29, 56] there has been no thorough review to confirm the validity of this approach. Equally, it is uncertain whether a CACC can perform as a CC when experiments are conducted with the chamber doors open although numerical simulations have been reported to show acceptable comparisons when the CACC front and rear chamber sides are open [80, 81]. Blomqvist et al. [13] compared ignition times using the CACC to the CC for 10 mm black PMMA at 50 kW/m^2 where the CACC tests used a chamber inflow rate of 160($\pm$5) L/min at 21 vol% O_2. The CACC tests had a $\sim$ 30% longer TTI and $\sim$ 10% lower peak HRR when the CACC tests were run without any sample preheating (no delay to test start in order to reintroduce a uniform chamber atmosphere). There are also few comparisons between the CACC and FPA data although good agreement in CO and CO_2 yields has been reported for heptane [63].

4. The Use of CACC Data in Numerical and CFD Modelling

There have been limited reported studies in which the CACC has been used to collect input data for CFD modelling. Beji et al. [18] used a closed-CACC to lower O_2 concentration to $\sim$ 2 vol% in order to prevent the ignition of liquid fuels and thereby decouple liquid heat up and evaporation from fuel combustion with the goal of improving computational sub-models without having to consider the complexities introduced by combustion reactions in the gas phase. There has been more work in the development of numerical models aiming to predict experimental outputs [52, 53, 82]. When using the CACC, the control of the atmospheric conditions alongside other variables presents a challenge when attempting to optimise the experiments necessary to fulfil the objectives of a study. This has led researchers to attempt to minimise the number of experiments necessary by incorporating polynomial approximations, for example the Doehlert matrix [83], to explore a certain number of variables, such as oxygen concentration and irradiance level [46, 84]. The interaction of these variables has been shown to complicate analysis of collected data. Variation of irradiance and oxygen concentration has been shown to change observed rates of charring, as well as the rate of char decay, leading to changes in other collected outputs such as CO and CO_2 production [48, 56].

The response surface methodology (RSM) as these polynomial approximations have been referred to in [26], has revealed interesting trends, such as the sharp increase in CH_4 concentration at higher heat fluxes for PIR foam, but early work featured no repeat experiments and no demonstration of predictive capabilities for polynomial models [48]. The initial works on polynomial models to improve predictive capabilities for confounding variables recognised the need to maintain pre-

dictive precision whilst also minimised the amount of experimental input into the grid domain. The models replicated experimental results well, unsurprising as these values had been used as input parameters, but the numerical and experimental uncertainty of its predictive capabilities was still great and therefore the proposals were still conceptual following the work of Hermouet et al. [52]. This limitation was significant since, as noted in [52], the main interest in the use of polynomial models for CACC data would be their predictive capabilities of variables between experimental data inputs. Later, this model was used to predict the burning of ABS at 50 kW/m^2 and 15 vol% O_2, in which the experimental test data was deliberately not included within the creation of the model in order to assess its predictive ability [53]. The results demonstrated a good match between independent experimental data and model predictions, but its practical applications were still questionable with only one prediction made with a large amount of input data required and no indications of the sensitivity to gaps in input data. Limitations on the current state of the art of polynomial models were summarised by Lundström et al. [85] in their review of different reaction-to-fire prediction models. They considered the number datapoints necessary for the model relative to its complexity an area requiring further research and a potential limitation should the number of datapoints, each requiring a separate experiment, be too great and therefore costly. Lundström et al. [85] also emphasised the importance of characterising the boundary conditions of the CACC such that the effect of the apparatus on the collected results, for example the radiation applied from the heated chamber walls, is accounted for when scaling data collected from the CACC.

5. Conclusions

This work has focused on the use of the CACC, and specifically, the motivation for its development and standardisation, key features of its design, as well as its future opportunities and limitations. A number of research gaps have been identified, which, should further research be undertaken, could improve apparatus scalability allowing for more meaningful comparison with larger scale tests. The CACC presents an opportunity to standardise an apparatus for the use of quantifying toxicity effluent. Its similarity to the cone calorimeter, a widely used method of determining HRR, is an attractive advantage to this method. However, based on the literature described within this review more work is needed to improve the control of conditions and sampling of toxic species.

The CACC was developed to allow researchers more control over the conditions under which sample burning took place. Whilst this is only of value for flammability and heat release in specialist circumstances, for example an oxygen reduction system [60], GER > 1 often represents the worst case when concerning toxic species. However, there appears to be limited consensus on the optimal method of CACC data collection, particularly with regards to the collection of toxic species production/yields. This can be partially explained by the different versions of the CACC that are in use. This is not simply a matter of whether the

CACC is open or closed but also the impact of the sampling collection point and mitigation of heat losses from the chamber walls. This lack of research consensus highlights the importance of standardisation through ISO/TS 5660-5 [10] as well as the recording of apparatus features, alterations to methodology and control variable settings used when reporting test results. This work has also highlighted the need for further research in order to improve the standardisation of the CACC.

5.1. CACC Research Gaps

In this paper, many features in the use of the CACC have been identified, which are worthy of further study. The following list of research gaps is not exhaustive, and there are many other worthy aspects of the apparatus for further study. However, some of the knowledge gaps identified during this review are listed.

Method of GER Control

- The advantages and disadvantages to each mode of oxygen reduction (vitiated/under-ventilated/mixed) should be further evaluated for the purpose of collecting toxic species from a range of materials.
- The sensitivity of global equivalence ratio measurements for various material types and thicknesses requires further study.
- Further comparisons are needed between the CACC and large-scale tests using an open-CACC with insulated walls and sampling from the CACC chimney.
- A comparative study between CACC featuring a chamber atmosphere of 21 vol% O_2 and standard CC for a range of materials.

Chimney

- Further study comparing toxic species production and sensitivity when the gas sampling probe (or a particle analyser) is located in the exhaust duct or the CACC chimney.
- Investigation into the sensitivity of toxic species to different chimney lengths to ensure that uniform mixing has been achieved when sampling from the chimney.
- Investigation into gas inflow and exhaust rates to determine the effect of these variables on species collection rates, including the effect of changes to density within the CACC chimney and the effect this has on species generation calculations.
- Further examination of the effect of quartz chimneys to allow the observation of flaming within the chimney.
- Study into the efficacy of a plate/flow restrictor, located at the chimney opening, for reducing the likelihood of PCO for a range of materials.
- The temperature of gases leaving the CACC chimney is of critical importance to understanding their oxidation when interacting with ambient air. Further research on gas temperatures at various operating conditions would be valuable.

- Study into toxicant deposition onto chimney walls and best practice for chimney cleaning frequency

Chamber

- A study into the impact of the CACC chamber on species deposition at different heat fluxes.
- Further research on methods to reduce heat losses from the CACC chamber, reduce load cell malfunction and implement a method of measuring gas temperatures within the chamber in order to allow greater control of conditions.
- A study into chamber reradiation and its effect on spectral irradiance uniformity onto the surface of the sample with and without added insulation to chamber walls.
- Further research on the effect of CACC chamber walls on the repeatability and reproducibility of the CACC at high irradiance levels.
- Oxygen concentrations within the chamber are not reported in the majority of published research. When reported, often only the deviation range from the intended target concentration is given. Analysis of the uniformity of oxygen concentrations within the chamber at various flow rates would be of value to understanding burning conditions.

Irradiance Level

- Further research to help identify CACC chamber atmosphere temperatures at various cone irradiances in order to define representative gas temperature criteria that allow the collection of better toxic species data by more accurately replicating global post-flashover compartment fire conditions.
- Further research into the effects of 'bubbling', charring and material regression on changes to received spectral irradiance through the increase/decrease of sample surface area, and how this can be mitigated to create steady-state burning conditions necessary for toxic hazard analysis.

Gas Inflow

- There is a lack of research into the effect of the gas inflow rate for materials other than pinewood sticks or PMMA in both vitiated and under-ventilated conditions. As the gas inflow has been shown to be critical to the position of flaming and the method of oxygen reduction a wider range of fuels should be studied.

As well as empirical research, there is a general lack of CFD modelling reported on the CACC performance. CFD studies on the effect of chamber reradiation and gas inflow rates would be of particular value for optimising the use of this apparatus. Additionally, researchers have reported findings from various supplementary attachments to the standardised CACC (for example, gas analysis using FTIR and particle size distributions using a particle analyser). Work is needed to define best

practice when using these attachments to promote further guidance in standards such as ISO/TS 21397:2021 [86]. For example, the location of the attachment's sampling point often varies between research making data comparison challenging. Furthermore, there is no repeatability or reproducibility round robin studies featuring data from the CACC, with or without, supplementary attachments. This is an important step for the full standardisation of ISO/TS 5660-5 and would greatly enhance confidence in the apparatus.

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Declarations

Competing interests The authors confirm that there are no competing interests that have directly or indirectly influenced this paper and its contents.

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