IMFSE Master Thesis Declaration

This form has been developed in the context of the unforeseen circumstances due to Covid-19, necessitating a reduction of practical project work (whether it be laboratory based, computational, or fieldwork) during the master thesis semester. It acts as a record of the impact on the master thesis. The form has been completed by the student and verified by the supervisor. **A copy of the signed form is included behind the abstract in the dissertation.**

Name: Robert Bray ___________________________

Work completed

All items of wholly, or partially completed work must be listed, indicating the percentage completion for each task. **Please take care to provide a full detailed list of all work done.**

26x bench scale tests using a cone calorimeter
26x bench scale tests using a controlled atmosphere cone calorimeter
2 weeks laboratory work were conducted
Data analysis and literature reviewed was not affected by the pandemic.

Work not commenced

Any items of outstanding work that have not been started should be listed here.

25x bench scale tests using a controlled atmosphere cone calorimeter which were due to test thicker samples at oxygen percentages of 15% and 17%.
1 week of laboratory time was lost due to the pandemic

Declaration

To the best of our knowledge, this form is an accurate record of the project status on (date)

Student: ____________________________________ (Signature)

Supervisor: Patrick van Hees____

HOST UNIVERSITY: Lund University

FACULTY: Faculty of engineering

DEPARTMENT: Division of fire safety engineering

Academic Year 2018-2020

Burning material behaviour in hypoxic environments:

An experimental study examining fire dynamics of composite materials in vitiated conditions

Robert John Bray

Master thesis completed at Lund University as part of the International Master of Science in Fire Safety Engineering

Supervisor – Prof. Patrick van Hees, Division of Fire Safety Engineering, Faculty of Engineering, Lund University, Sweden

Promoter(s): Patrick van Hees

Master thesis submitted in the Erasmus+ Study Programme

International Master of Science in Fire Safety Engineering

DISCLAIMER

This thesis is submitted in partial fulfilment of the requirements for the degree of *The International Master of Science in Fire Safety Engineering (IMFSE)*. This thesis has never been submitted for any degree or examination to any other University/programme. The author declares that this thesis is original work except where stated. This declaration constitutes an assertion that full and accurate references and citations have been included for all material, directly included and indirectly contributing to the thesis. The author gives permission to make this master thesis available for consultation and to copy parts of this master thesis for personal use. In the case of any other use, the limitations of the copyright have to be respected, in particular with regard to the obligation to state expressly the source when quoting results from this master thesis. The thesis supervisor must be informed when data or results are used.

Read and approved,

Robert John Bray

27/04/20

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I would also like to thank my family for their support and assistance throughout this project. This work is dedicated to my Uncle Malcom Munday who sadly passed away during its formation. His commitment to serving his local community, both in his spare time through volunteer work and his work life in the probation service, ensures that he leaves behind a proud legacy. The continued strength and bravery of his immediate family during these difficult times also serves as a reminder of their inspirational spirit.

List of abbreviations

ORS – Oxygen reduction system

CC – Cone calorimeter

CACC – Controlled atmosphere cone calorimeter

ABS - Acrylonitrile butadiene styrene

PMMA – Polymethylmethacrylate

PE – Polyethylene

PP – Polypropylene

PS – Polystyrene

HRR – Heat release rate

MARHE – Maximum average rate of heat emission

MLR – Mass loss rate

HOC – Heat of combustion

HIPS – High impact polystyrene

FPA – Fire propagation apparatus

LOI – Limiting oxygen index

LOC – Limiting oxygen concentration

SWNT - Single walled carbon nanotubes

FMRC – Factory mutual research corporation

QC – Quartz chimney

MC – Metal chimney

HRRPUA – Heat release rate per unit area

Nomenclature

Literature Review Part 1

χ	flame radiative fraction radiated to the environment	$\dot{q}''_{s,c}$	In depth conduction (J/gm^{2}s)
ΔH_c	Heat of combustion (J/g)	$\dot{q}''_{s,r}$	Surface re-radiation (J/gm^{2}s)
$Y_{O_{2,\infty}}$	Mass fraction of oxygen in ambient conditions	$\dot{q}''_{f,r}$	Radiative feedback of the flame (J/gm^{2}s)
υ_s	Oxygen-fuel mass stoichiometric ratio	$\dot{m}''_F$	Rate of fuel vaporisation per unit area (g/cm^{2}s)
$C_{p,\infty}$	Specific heat at constant pressure (J/gK) in ambient conditions	f	Fraction of heat released that is transferred back to the fuels surface
T_p	Pyrolysis temperature of the solid fuel (K)	$\dot{m}''$	Burning rate per unit area
T_∞	Ambient temperature (K)	$\dot{Q}''_E$	Externally applied heat flux
ΔH_P	Heat of gasification (L+$C_p(T_p$-T_∞)) (J/g)	$\dot{Q}''_L$	Heat lost from the surface
Q	Normalised non-convective heat transfer at the surface	L_v	Heat of gasification
$\dot{q}''_c$	Convective heat transfer rate	ϕ	(Fire point theory) fraction of heat loss from a flame to cause extinction
$\dot{m}''_c$	Rate of flow of fuel into the flame under critical conditions	$\dot{m}''_{cr}$	Critical mass flux at extinction
$\dot{m}''_{ideal}$	Ideal mass loss rate where there are no heat losses (measure of burning intensity)		
h	Convective heat transfer coefficient [W/(m2·K)]	L	Characteristic length [m] of the material
K	Thermal conductivity of the body [kW/(m·K)]	α	Thermal diffusivity ($\frac{k}{\rho c}$)
ρ	Density (kg/m^3)	c	Specific heat capacity (J/kg.K)
Y_o	Mass fraction of oxygen in atmosphere		
$\dot{q}''_g$	Heat release rate per unit area in the gas phase	$\dot{m}''_{O,B}$	Mass loss rate of oxygen consumed through burning
$\Delta H_{C,F}$	Heat of combustion of fuel burnt	C_{pg}	Specific heat capacity

$\dot{m}''_{F,B}$	Mass loss rate of fuel burnt	T_F	Temperature of the fuel
T_∞	Temperature (ambient)	$\dot{q}''_e$	Energy feedback per unit area
μ_g	Dynamic viscosity	C	Constant taken as unity in Equation 14
p^n	Ambient pressure	A_g	Pre-exponential factor for reaction rate in the gas phase
B	Spaldings B number	Le	Lewis number $(\lambda_g/\rho_g C_p D_g)$
ρ_g	Density of the gas phase	U_m	Velocity of the opposed gas flow
D_g	Gas mixture averaged diffusion coefficient	λ_g	Thermal conductivity

Literature Review Part 2

$\dot{q}$	Heat release rate (kW)	$X_{O_2}^0$	Initial value of oxygen analyser reading
Δh_c	Net heat of combustion $(kJ \cdot g^{-1})$	X_{O_2}	Oxygen analyser reading, mole fraction of oxygen
r_o	Stoichiometric oxygen/fuel mass ratio	t	Time (s)
C	Orifice flow meter calibration constant $\left(m^{\frac{1}{2}} \cdot g^{\frac{1}{2}} \cdot K^{\frac{1}{2}}\right)$	t_d	Delay time on the oxygen analyser (s)
Δp	Orifice meter pressure differential (Pa)	$X_{O_2}^1$	Oxygen analyser reading, before delay time correction
T_e	Absolute temperature of gas at the orifice meter (K)	E	Average value of the net heat release per unit mass of oxygen consumed
E_{CO}	Net heat release per unit mass of oxygen consumed for CO (17.6kJ/g_{o_2})	ϕ	Oxygen depletion factor
X_{CO}^A	Measured mole fraction of carbon monoxide in the exhaust gases	$X_{O_2}^A$	Measured mole fraction of oxygen in the exhaust gases
$\dot{m}_e$	Mass flow rate of exhaust duct	α	Chemical expansion factor
M_{O_2}	Molecular weight of oxygen	M_a	Molecular weight of air
$X_{H_2o}^0$	Mole fraction of water vapor in the incoming air	$X_{O_2}^{A^0}$	Measured mole fraction of oxygen in the incoming air
$X_{CO_2}^A$	Measured mole fraction of carbon dioxide in the exhaust gases	$X_{CO_2}^{A^0}$	Measured mole fraction of carbon dioxide in the incoming air

γ	Thermal expansion factor, time dependant	$X_{O_2}^{A^s}$	Measured mole fraction of O_2 in the surrounding air
$X_{H_2O}^{S}$	Measured mole fraction of H2O in the surrounding air	$\tilde{\gamma}$	Thermal changeable dilution factor, time dependant
$\dot{m}_e^0$	Mass flow rate in the exhaust duct prior to the test	m_g^B	Mass flow rate of the incoming gas mixture to the enclosed box

Methodology

$\dot{V}_T$	Total flow rate (l/min)
$\dot{V}_N$	Flow rate in nitrogen (l/min)
$\dot{V}_A$	Flow rate in air (l/min)
C_{O_2}	Desired oxygen concentration (%)

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Abstract

The progression of fire safety research has contributed to improving the guiding principles of standardised building design. Research making use of pure materials, once common in homes and workplaces, are less relevant as such materials are no longer as prevalent. It is often newer, composite materials that are featured more prominently in building contents. The trend towards the evolution of commonly found materials introduces greater uncertainty into assumptions frequently made in simplified calculation methods.

Hypoxic conditions, where oxygen concentrations within an enclosed environment are lowered in order to reduce the ignitability and flammability of the room's contents, are less frequently tested. Systems that create hypoxic conditions, referred to as Oxygen Reduction Systems (ORS), are typically used to protect high value or high-risk contents. High-loss fire scenarios and less rigorously validated research data supporting system design introduce the need for further insight.

It is the primary intent of this thesis to contribute to the discussion of small-scale material testing in hypoxic conditions. Acrylonitrile butadiene styrene (ABS) samples of various thicknesses (20mm, 10mm and 5mm) have been compared to a composite mix of ABS with a surface layer of cardboard and secondary layer of bubble wrap. Tested materials were considered reasonable because they represent a plastic commonly used in the formation of high-end electronic devices whilst cardboard and bubble wrap layers represent common storage components. The samples have been tested with exposure to radiant heat fluxes, namely 25kW/m^2, and 50kW/m^2. The oxygen concentrations compared are 20.95%, 17% and 15%.

Analysis found that due to unique material behaviours in composite samples, caused by an ash forming top layer, heat release rates for hypoxic conditions could be greater than those in ambient conditions. It is argued that unique variations in composite material behaviour limit the validity of tests of pure materials in isolation from their wider application within an ORS design.

Section 1 - Introduction

Section 1 Part 1 - Motivations

Material burning behaviour in hypoxic conditions is a research topic that suffers from the same limitations and challenges as found in research on material burning behaviour in ambient conditions. Numerous studies, such as the work by Schartel(1), comment on the difficulties of comparing test data from bench scale experiments due to the variation in boundary conditions applied to the samples tested. Some such variables that limit the direct comparison of results include sample thickness, exposed heat flux, ignition source, sample holder design and distance from the cone heater. This inexhaustive list highlights one of the many challenges facing researchers when conducting research and comparing results to previous work, the compatibility of bench-scale data between samples. Material testing in hypoxic conditions is also further impaired by the limited range of test data currently available due to the specialist nature of ORS (Oxygen Reduction Systems) making use of reduced oxygen environments.

The motivation of the following thesis is to contribute research data on material burning behaviour under hypoxic conditions in such a way that new insights can be gained in order to further improve the application of ORS system testing and design. The focus of the thesis on hypoxic conditions is partly due to the limited extent of available research data as previously noted. Equally, it is because of the potential benefits such systems can deliver to high value and high-risk contents in the right contextual environment.

It is frequently the case that fire protection and prevention systems are used within industrial settings in order to mitigate against the foreseeable risk of fire. The use of ORS's has been explored as a potential alternative to sprinkler systems (2). Such systems also have the benefit of reducing the likelihood of ignition events due to the lower concentration of O_2 available within the relevant protected space. ORS could reduce the likelihood that a fire starts in the first place (as such acting as a prevention system) or reduce and confine the fire growth where a fire does occur (as such acting as a protection system).

However, recent studies on the effectiveness of imposed O_2 concentrations at preventing ignition as well as suppressing fire spread have indicated that regulatory standards (VdS 3527, 2007 (3) and EN 16750, 2017 (4)) have overestimated the effectiveness of the imposed conditions on achieving the intended mitigatory effect (5). Also, it is clear from research that the introduction of oxygen depleted environments does not ensure that a satisfactory replacement for fire protection systems, such as sprinklers, is achieved as discussed by Zhou et al (6).

Clearly ORS present an adaptable and potentially effective form of mitigation to fire risk but there has been some doubt over the current applications (5) (6), limitations and design specifications that are considered acceptable. In order to provide a viable alternative to other fire prevention and protection systems, which are available to designers and clients, further research is needed. This is not simply because there is a lack of usable data available to form the basis for effective regulatory standards, but also because the range and limitations of suitable usage for an ORS is not yet sufficiently captured. Design teams cannot make informed decisions where installing such systems in certain environments due to insufficient quantity of data covering design variables. Research on the effect of material orientation, ignition source, imposed heat flux, composite layers of materials and aerated cavities of storage containers form an inexhaustive list of potential variables insufficiently considered.

Oxygen depleted environments used to prevent or reduce fire spread are not suitable in all design situations. For example, the effect of such environments on human health will often discount their use in highly populated spaces. Additionally, the difficulty of achieving and controlling a satisfactory O_2 percentage in well ventilated, large spaces could also prove an insurmountable disadvantage in many cases. Despite this, there are sufficient instances where such systems would prove to be of benefit, that pursuing further research is desired. The following thesis aims to conduct experiments in order to analyse material behaviour in low oxygen environments. By providing further data on the subject of hypoxic fire behaviour the thesis aims to advance the development of regulatory standards as well as to supplement the knowledge of designers when installing oxygen reduced systems.

The present study focuses on the polymer acrylonitrile butadiene styrene (ABS) along with multiple layers of a composite packaging build-up involving common storage materials. Whilst there are more common polymers used within the built environment ABS has been selected for a number of reasons. Some of the more common polymer types (PMMA, PP, PE) have received significant attention in similar studies using controlled atmosphere cone calorimeters (CACC) and their typical burning behaviour is well known. Due to its common use and predictable burning behaviour there is a large collection of data related to PMMA (polymethylmethacrylate) in reduced oxygen environments (7) (8) (9). Similarly, PE (polyethylene), PP (polypropylene) and PS (polystyrene) have also received both theoretical and experimental discussion in the works of researchers such as Tewarson et al(10), Tewarson et al (11) and Kashiwagi(12). Some works have discussed ABS in great detail but often within the context of polymer degradation at much lower temperatures, only slightly above ambient, within atmospheric oxygen concentrations and without the use of a cone calorimeter (13). Other studies have considered ABS in hypoxic conditions and have used CACC equipment to conduct experiments but have discussed the resulting data from a much broader perspective often considering a multitude of plastics with conclusions drawn from wider comparisons rather than focussed analysis of ABS (14) (15). After an extensive study of available literature only one research article directly focussed on ABS exposure in a CACC, the work of Hermouet et al (16). The article exclusively discussed ABS experimental data produced by a CACC under hypoxic conditions and irradiance levels relevant to the current study. However, the material thicknesses used in the work of Hermouet were markedly different between the tests undertaken in this study so will provide useful supplementary comparison between the works conducted. Composite sample testing in hypoxic conditions was also limited with only data from one composite panelling system being identified (the work of Marquis and Guillaume, [17]) which tested similar irradiance and oxygen levels but not ABS, cardboard or bubble wrap.

As well as limited comprehensive coverage of ABS under reduced oxygen conditions, compared to other common polymer samples, ABS also features heavily in the production of high-end electronic goods. One of the primary reasons for the polymer choice in this instance was made through the consideration of the goods that are considered most reasonably, commonly associated within ORS systems. According to the website of an international ORS system installer (N2ORS, [18]) ORS systems are typically installed in high hazard warehouse facilities such as chemical plants and paper mills, IT and data centres or archive centres such as libraries. Other common polymers are more often used in wider society, but their application is typically for cheaper, more reproducible items which are not often protected within ORS systems. Examples include, PS which is most often associated with yoghurt pots or vending machine cups or PP which is often used for bottle caps or bowls as well as in film form for crisp packets (British Plastics Federation, [19]). The use of PE and ABS are both much more suited to applications usually associated with data centre facilities with PE often being used for cable insulation and ABS forming the covering for high quality electronic devices due to its antistatic performance, wear resistance and decorative finish.

ABS was also used as part of the composite arrangement tested within the work conducted. The tested arrangement does not represent one product but rather represents a typical combination of materials that may be present within data centres protected under ORS systems. Cardboard with multiple underlying layers of bubble wrap is a common combination of storage items typically used to store fragile items, such as high-quality electronic goods. This composite arrangement is therefore considered relevant in the examination of composite samples in ORS. By using ABS within this arrangement, there is also the potential for direct comparison with the pure material also tested.

It is not the intent of the current study to directly examine the performance of ORS testing regimes as given in the regulatory standards reviewed as part of this work. As such, the proposed testing materials are not arranged as per the guidance of these standards, but rather, have been chosen in order to collect data on material behaviour where limited data currently exists.

The small-scale samples used in a cone calorimeter are not representative of a full-scale storage package as would be seen within the protected enclosure of an ORS. As the following quote by Babrauskas(20), as paraphrased by Schartel(21), notes;

> ‘*The cone calorimeter setup was developed thoroughly to target the properties of materials rather than to correspond to a special full-scale scenario of a real fire.*’.

It is reasonable therefore to consider the composite sample as reflective of the potential impact of more complex materials featured within ORS enclosures rather than testing pure sample materials in isolation but at the same time recognising that it is not indicative of a direct comparison with a storage package within an ORS. The addition of bubble wrap may also produce some interesting results due to the aerated release of ambient air into the composite cavity introducing a minor, local increase in O_2 volume at the point of localised burning. The lack of research data on bubble wrap also offers a good justification for its inclusion in a composite arrangement in this instance.

Section 1 Part 2 – Objectives

Leading on from the necessary motivation for the project and the proposed tested materials the targeted objectives of the thesis are;

- Investigate the resulting effects of various imposed heat fluxes on material burning behaviour in a reduced oxygen environment in which a range of O_2 concentrations are compared.
- Investigate the resulting effects of fuel type on material burning behaviour in a reduced oxygen environment in which a range of O_2 concentrations are compared.
- Investigate the resulting effect of an aerated cavity within a compound sample on material burning behaviour in a reduced oxygen environment in which a range of O_2 concentrations are compared.
- Investigate the resulting effect of a material thickness on material burning behaviour in a reduced oxygen environment in which a range of O_2 concentrations are compared.

For the purpose of this study the material burning behaviour refers to heat release rate (HRR), mass loss rate (MLR), time to ignition, CO_2 yield, smoke production and CO yield. The study will make use of a cone calorimeter and a controlled atmosphere cone calorimeter. The used testing apparatuses have been justified based on their wide usage within the fire research community. Additionally, oxygen calorimetry is thought to be one of the most useful bench scale testing methods for material behaviour in forced fire conditions (Morgan et al. (14)). 52x tests were conducted on samples with 26x on pure ABS and 26x on the composite layered sample. Prior to experimental work a literature review was conducted with resulting discussions in Section 2. The laboratory methodology is discussed in Section 3 and the thesis concludes with data reporting and subsequent analysis in Sections 4 and 5.

The following literature review has been conducted over the timescale of the project and has been conducted in a narrative approach. Research articles and reports were predominantly sourced from free academic search engines, references of articles read previously, and recommended articles from the Lund University supervisory team. Theoretical discussions made focus on the primary theories discussed by researchers on the topic of hypoxic burning behaviour. These theories are non-exhaustive and have been prioritised for inclusion in theoretical discussion due to their prominence in the academic literature reviewed. The study does not note all theories on the subject due to the limited size of the final thesis document.

Section 2 - Literature Review

Section 2 Part 1 – Fire behaviour of materials in hypoxic conditions

Section 2.1.1 - Material burning theory

In order to understand burning behaviours of materials in both typical atmospheric and hypoxic conditions numerous research articles were reviewed. It is considered most appropriate to initiate discussion by covering theories relating to the ignition and sustained burning of fuel. Early research in the field of fire science focussed on characterising models that explained the general properties of material burning as well as the balance between heat production and heat losses. One such commonly used theory is Spaldings B number, first proposed in 1950, which is a concept that simplifies the treatment of material degradation in the condensed phase through the use of a thermal model. The theory, which is also referred to as the global heat of vaporisation concept, is a simplification that only considers steady state burning. This steady state limitation is described by Kashiwagi (12) as preventing its use for most materials, which burn in such a way that they are considered time dependant, and therefore the model required further adaption prior to use outside of the vaporisation of steady state, liquid fuels. In fact, the B number was originally introduced to model the characteristic behaviour of liquid fuel droplets. A form of the B number is given by Emmons (22) as;

$$B = \frac{(1-\chi)\left(\Delta H_c Y_{O_{2,\infty}}\right)/v_s - C_{p,\infty}\left(T_p - T_\infty\right)}{\Delta H_P + Q} \qquad \text{Equation 1}$$

The B number represents a material property during combustion which determines the conditions at the fuels surface and giving a modelled prediction of the mass transfer from the fuels surface. It can be seen that the numerator contains values that relate to the environment and material properties whilst the denominator contains heat losses from the combustion process. Evidently the model contains the burning surface temperature, the specific heat of the material and the heat of combustion. The value Q within the B number equation, which represents the heat transfer at the surface of the material, can be calculated using the following equation;

$$Q = \frac{\dot{q}''_{s,c} + \dot{q}''_{s,r} - \dot{q}''_{f,r}}{\dot{m}''_F} \qquad \text{Equation 2}$$

Whilst the B number represents a simplified model for sustained burning it is an important concept because it identifies many of the terms that are critical variables in cone calorimetry, as discussed in Section 2 Part 2: Equipment Study. For example, the heating potential terms defined in the numerator of Equation 1, demonstrate the importance of the material properties (via ΔH_c and $C_{p,\infty}$), atmospheric conditions (via $Y_{O_{2,\infty}}$ and T_∞) and fire characteristics (via χ and T_p). As described by Rangwala(23) over the proceeding decades (more specifically the 1980's and 90's) engineering correlations were used to convert the steady state B number theory into a time dependant engineering approximation for material behaviour. Typically, this involved studies that discounted the Q value (representing the heat losses to the surface and therefore being conservative by considering adiabatic conditions) or incorporated the heat losses but as a constant value. For example, Tewarson et als 1981 paper(24) attempted to correct for radiative losses in burning fuels (solids and liquids) by using engineering corrections. The results of which still yielded a range of accuracies of convective heat flux of the flame at 30% deviation and radiative heat flux of the flame at 20% deviation (Tewarson et al(24)). In Rangwala's 2008 study however the need to calculate the Q value was avoided by calculating heat losses implicitly through the methodology for obtaining standoff distances via experimental measurements as first proposed by Torero et al(25).

The development of the B number theory was an important step in determining the spread of flame over a materials surface and the necessary factors that would affect the rate at which pyrolization would occur. In the 1970's the work of Rasbash expanded the topic further (26). The following quote describes the theoretical deviation taken through the development of his work on the fire point theory;

> *'An understanding of spread of flame over surfaces is of major importance in fire science. A number of theories of flame spread have been put forward, both in liquid and solid fuels. These theories are, for the most part, fuel orientated and focus on the rate at which fuel becomes heated to a certain temperature that characterises the onset of flame. I suggest that it may also be illuminating to focus on the flame as well as the fuel'*
>
> D.J Rasbash in A flame extinction criterion for fire spread, 1976(26)

The fire point theory explored the conditions necessary for sustained burning as well as flame extinction in materials. A sustained burning rate in a solid fuel using the fire point theory is described in the following equation as documented by Beyler (27);

$$\dot{m}'' = \frac{f\Delta H_c \dot{m}'' + \dot{Q}_E'' - \dot{Q}_L''}{L_v} \qquad \text{Equation 3}$$

Rasbash acknowledged the work Spalding's B number procedure (Rasbash, (26)) but also intended to capture the influence of chemical kinetics of the flame reaction and the limit conditions that would impact it. This involved the formation of the term ϕ which is defined by Beyler (27) as the fraction of heat from the flame which is to be lost such as to cause flame quenching and thereby extinction. It had long been known that flame extinction would occur when flames reached a certain lower flammable limit (LFL). Burgess and Wheeler (28) had reported that for many hydrocarbons the adiabatic flame temperature at the LFL was approximately 1600K. As reported by Beyler (29) the work of White (30) further consolidated this finding by confirming that even where the initial material temperature was increased, the adiabatic flame temperature would remain consistent (at around 1600K). Rasbash (26) concluded that such consistent adiabatic flame temperatures could be explained by the consistency of flame extinguishment in hydrocarbons based on the limiting conditions to which they were exposed to. In his 1975 paper on fire point theory the following equation was used to describe the limiting conditions of the flame front as it interacted with a burning material;

$$\dot{q}_c'' = \phi \Delta H_c \dot{m}_c'' \qquad \text{Equation 4}$$

The convective heat transfer rate, $\dot{q}_c''$, represents in this instance the flames rate of heat loss. For many hydrocarbons the critical flow rate of fuel and the heat of combustion of its fuel vapours are comparable and therefore the ϕ is subsequently in the range of 0.1 to 0.4 (Tewarson, (31)). Flame extinction therefore becomes a balance between the production of heat from the combustion of the fuel and the heat losses from the flame to its surroundings. This is captured by the following equation as reproduced by Beyler (27) in which the heat losses are described by the fractional heat losses in the term ϕ. As the sum approaches 0 extinction is achieved.

$$(\phi\Delta H_c - L_v)\dot{m}''_{cr} + \dot{Q}''_E - \dot{Q}''_L = 0 \qquad \text{Equation 5}$$

The fire point theory was an advancement of the academic understanding of material burning behaviour because it expanded research beyond focus on fuel parameters to include the flame itself and the limiting conditions to which the flame was exposed to.

Whilst progress had been made on the burning regime of condensed materials, through consideration of both material and flame boundary conditions, no methodology of quantification for burning intensity had yet been proposed. In 1976 Tewarson and Pion(32) proposed the following 'measure for burning intensity of a material';

$$\dot{m}''_{ideal} = \frac{\dot{Q}''_F}{L_v} \qquad \text{Equation 6}$$

Similarities can be noted between Equation 6 and Equation 3 as the value $\dot{Q}''_F$ is equal to $f\Delta H_c\dot{m}''$. In Equation 6 the applied heat flux and heat losses have been removed to represent the fuels behaviour if all heat losses were reduced to zero. These adiabatic conditions therefore represent the maximum burning rate of the material and therefore allow materials to be ranked by burning behaviour. However, as recounted by Drysdale (33), such equations at small scale do not effectively capture the radiation dominant burning behaviours of larger fuel sources. Increasing sample size had been demonstrated by Markstein(34) to increase sample emissivity by approximately 3x in a sample of PMMA where the diameter of the sample was increased from 0.31 to 0.79m. This was rectified in the work of Tewarson (24) by increasing the oxygen concentration in small scale samples and thereby ensuring that radiation became the dominant form of heat transfer.

As the measurement of burning material did not effectively account for radiative dominance that would be observed in larger samples relative to small scale samples a combustibility ratio was defined. The combustibility ratio relies upon the large impact of $\frac{\Delta H_c}{L_v}$ where compared to the relative range of χ found in most hydrocarbons. As shown Equation 7 the impact of sample area has been removed allowing for comparative ranking without the variable of sample size. The combustibility ratio, $\frac{\Delta H_c}{L_v}$, therefore gives a simplified method of ranking materials originating from the heat release rate properties previous research had defined.

$$\frac{\dot{Q}_c}{A_F} = \dot{Q}''_{net}\chi\left(\frac{\Delta H_c}{L_v}\right) \qquad \text{Equation 7}$$

Section 2.1.2 - Discussion of properties relevant to material burning behaviour

With the basic principles of material burning outlined it is appropriate to note the factors which have been shown to influence sample burning behaviour. One variable which is of particular interest to the current study is the thermal thickness of the sample. Early studies of material behaviour when exposed to an irradiance and a piloted ignition source had shown that the necessary intensity of ignition to cause sustained burning was greater when the material density was higher and that there was a temperature gradient within the sample (Simms, (35)). This can be linked to the relative thermal thicknesses between samples. A sample is considered thermally thick, also referred to as a semi-infinite solid, where there is a thermal gradient within the sample due to an imposed heat flux on one side of the sample. A sample is considered thermally thin when there is no thermal gradient and the sample is a uniform temperature. The use of the biot number to distinguish between thermally thick and thermally thin samples is evident in early analytical works of material burning behaviour (Simms, (36)). The biot number is defined as;

$$\frac{hL}{K} \qquad \text{Equation 8}$$

The biot number is the ratio of heat transfer resistance within the solid to heat transfer resistance at the surface of the solid. Biot numbers smaller than 0.1 indicate thermally thin samples whereas larger numbers indicate thermally thick samples (Drysdale, (33)). The methodology used to calculate heat transfer through the solid for thermally thin and thermally thick samples is different. The thermal thickness of a sample can be determined via the following calculation which, if true, confirms that the sample is thermally thick;

$$\frac{L}{2\sqrt{(\alpha t)}} \approx 2 \qquad \text{Equation 9}$$

Where;

$$L > 4\sqrt{(\alpha t)}$$

It is noted that the thermal diffusivity of the material is necessary to define its thermal thickness. Thermal diffusivity is defined as;

$$\alpha = \frac{k}{\rho c} \qquad \text{Equation 10}$$

The influence of thermal thickness is a significant factor in material burning behaviour that can be further understood by the properties that form thermal diffusivity. The thermal diffusivity quantifies the materials propensity to either resist or promote thermal equilibrium when exposed to a change in applied heat flux at its surface. As shown in Equation 9 the characteristic length and time of exposure are also important factors when determining the temperature gradient within a solid. This poses a particular challenge when analysing cone calorimeter (CC) data because of the multiple uses of the equipment. Not only is the CC used to rank the ideal performance of materials by their basic properties, for example the effective heat of combustion, but it is also used to conduct applied research and product development. Applied research often requires the testing of a representative sample from which it is considered reasonable to assume performance as per the final installed arrangement. Evidently many smaller samples will have a much smaller characteristic length and will be thermally thinner than the final installed material which will affect the time to ignition of the tested sample, as noted by Babrauskas (37). Whilst ISO5660 proposes unique procedures for samples of 6mm and below there is some evidence to suggest that, for certain materials, the fundamental performance of the material has been found to change. For example, the work of Kashiwagi et al (38) demonstrated that the behaviour of a fire-retardant layer of PP nanocomposites in thermally thin samples changed compared to thicker samples as the intumescent layer required a certain time delay in order to activate. The thermally thin sample did not offer a sufficient time effect and therefore the performance of the fire-retardant layer was not effectively accounted for by the CC. Further to this, Schartel et al(39) highlighted how the thickness of CC test samples effected different types of materials in different ways depending on the reaction to burning (charring, residue forming, melting etc.). Using previously recorded test results Schartel et al (40) demonstrated that a 15% increase in Mg(OH)2 (by material weight) in a high impact polystyrene (HIPS) sample saw charring behaviour of samples tested at 3mm and 6mm. With 15% less Mg(OH)2 dramatic changes to material burning behaviour were observed with the 3mm sample no longer demonstrating charring behaviour.

It is clear that material inconsistencies are a risk to the applicability and comparability of test data from bench scale cone calorimetry particularly when such data is to be used for product development.

This risk is further compounded due to other variable factors that can influence the burning behaviour of test samples. Such variables can originate from material properties, geometric considerations and environmental conditions. For example, the surface orientation of samples has been shown to influence burning behaviour. Some regulatory standards require that samples are tested in both horizontal and vertical orientations (PAS95: 2011) to account for the differences in potential sample performance. There has been a general consensus in the literature reviewed that, for low oxygen environments, the horizontal orientation of samples demonstrates a more significant flame spread reduction, compared to ambient O_2 concentrations, than vertical orientations. Rasbash and Langford (41) tested wooden cribs in FPA apparatus in both horizontal and vertical orientations and noted the difference in burning behaviour due to the different modes of heat transfer employed in each case. For upward burning in vertical samples the primary mode of heat transfer was convection whilst for horizontal burning in the horizontal samples the primary mode of heat transfer was from radiation. During the experiments it was also noted by Rasbash and Langford that the size of flames as they extinguished in horizontal cases was extremely limited (1cm thick) whilst in the vertical cases flames were of a 'quite substantial' size before suddenly extinguishing. In horizontal samples it was concluded that extinguishment occurred because of the flame spread rate being insufficiently fast to cover volatile production. For the vertical samples the researchers concluded that extinguishment had occurred due to chemical factors insufficiently compensating for heat losses. The influence of mode of heat transfer on a sample can be observed in Tewarson and Ogden's 1992 paper (42) on the fire behaviour of PMMA. It is illustrated in Figure 1 that where the O_2 concentration is lowered in a horizontal sample the convective dominance of heat transfer increases. As horizontal samples are more reliant on radiation to promote heat transfer a reduction in radiation due to O_2 concentration in the local atmosphere has more impact on horizontal samples performance. It can therefore be concluded that in some cases, where examining flame spread along the surface of a material in a hypoxic environment, it would be more suitable to examine vertical samples where flame spread rate is less effected by the hypoxic conditions to determine information on worst case performance of the material.

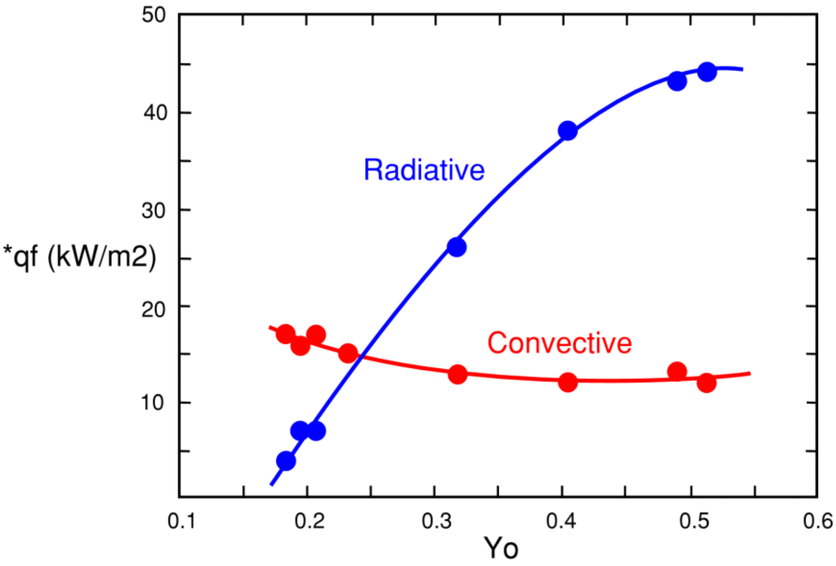


Figure 1 Flame radiative and convective heat verses oxygen mass fraction for combustion of 10mm, 25mm horizontal PMMA slab (redrawn from Tewarson et al. 1981(11))

This is commented upon in Tewarson and Ogden [(42)] where describing the erroneous results of the ASTM standard test for determining oxygen index (ASTM D2863-70 – 1970). In this test the vertical sample was ignited at the top and downward burning was monitored with the limiting oxygen index (LOI) determined at the oxygen concentration where the flame was extinguished. However, as noted by Tewarson and Ogden, downward flame spread is reliant on solid phase heat conduction. Due to the particular radiation and flow characteristics acting on the sample the ASTM test gave an inaccurate LOI of Y_O =0.194 rather than Y_O =0.178, as had been previously theoretically and experimentally calculated. Both the position of the ignition source, which partly determines the direction of burning observed, and the sample orientation have an impact on LOI in small scale testing.

A study conducted by Xin and Khan [(9)], which was conducted using FPA apparatus, also tested a range of materials in both horizontal and vertical orientations (although the vertical arrangement was two parallel panels rather than one vertical panel as shown in Figure 2). Results from this study suggested that horizontal samples gave similar LOC than the vertical, parallel samples and were often more conservative by giving a lower LOC. For example, horizontally arranged PMMA had a LOC of $Y_O = 10.6\%$ whereas the parallel sample had a LOC of $Y_O = 14.7\%$. Collectively, research seemingly suggesting that whilst vertical samples provide a higher rate of flame spread, they also often give higher, less conservative, indications of LOC. Evidently, the limited research conducted on CACC sample orientation suggests that the observation aims of the research are paramount to the decisions regarding which orientation represents the most conservative test arrangement. Xin and Khan [(9)] conclude that the results of horizontal samples are applicable to parallel panel configurations due to the closeness of LOC results. This seems to be a premature statement as the sample selection is limited, the comparability of data is limited to LOC only and the closeness of LOC is debatable and subjective.

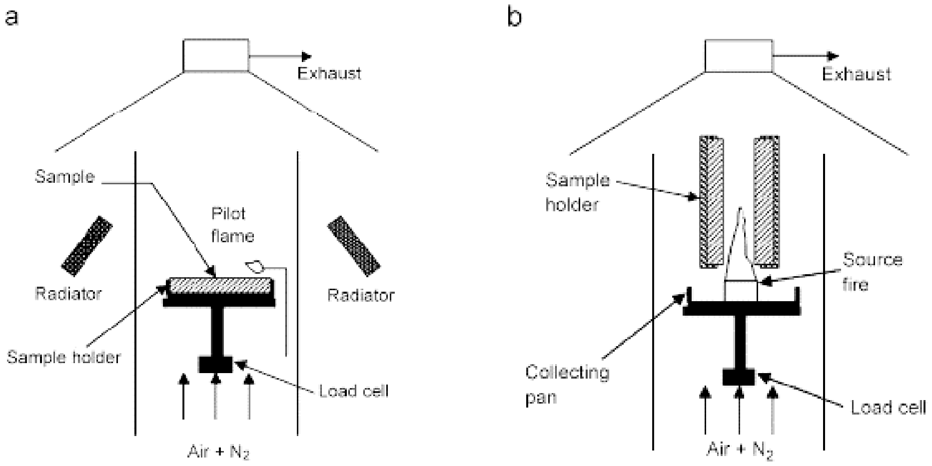


Figure 2 Experimental set up (a horizontal. b vertical parallel samples) (Xin and Kahn, [(9)])

Throughout the literature review another critical contributor to material behaviour in hypoxic conditions was through the imposed radiant heat flux applied via cone heaters during testing. Experiments performed in ambient and hypoxic conditions consistently demonstrated that a higher imposed heat flux would decrease the time to ignition and increase peak heat release rate (HRR) of samples Morgan and Bundy[(14)]. Numerous studies on different materials indicate that a higher imposed radiant heat flux would reduce the LOC necessary to sustain the pyrolisation of solid fuels Xin and Kahn[(9)], Delichatsios[(43)]. Such correlation was not shown without limits however, Xin and Khan [(9)]

concluded that applying heat fluxes to samples had a significant impact on the LOC until heat fluxes above 30kWm^2 which had no further impact on LOC. There is some discussion regarding the potential influence of external radiant heat flux by Tewarson (11) based on his observations of data collected by Kashiwagi (44). Tewarson notes that during flame extinction caused by reducing oxygen mass fraction flame heights decrease rapidly, heat release rates via convection increase and heat release via radiation decrease. The reduction of radiation at the sample surface is an important factor for flame extinction and Tewarson noted that there '*may be a coupling between the change in the flame shape, attenuation of radiation by vapours near the surface, and the total available heat*.'. The effect of providing an external radiant heat flux onto a sample during testing seemingly delays the natural effects observed in the flame behaviour. The natural effects, i.e. the reduction of radiative heat release rate, are delayed by providing supplementary radiative heating onto the sample. This prevents the premature extinguishment of samples, due to insufficient transfer of heat to maintain combustion rather than a lack of O_2 to sustain combustion, that presents misleading indications of LOC. As noted by Xin and Kahn(9) however, the effect of supplementary irradiation is limited as preheating the material does not reduce the LOC beyond its true value caused by the theoretical yield of O_2 necessary to sustain combustion. This is supported by the research of Hermouet et al. (16) which tested ABS samples in a CACC at heat fluxes ranging from 20kW/m^2 to 50kW/m^2. At certain oxygen concentrations the heat flux was shown to cause ignition where lower heat fluxes had not, for example samples at 12.5% mass fraction ignited at irradiance levels of 35kW/m^2 but not 20kW/m^2.

It should be briefly noted that studies have shown that overall sample width has been shown to influence material behaviour particularly with regards to rates of flame spread and flame heights. A study by Pizzo et al(45), where PMMA slabs were tested vertically at various widths, found that samples with widths of 100mm or more do not affect the material behaviour for flame heights, heat release rates per unit widths and rate of flame spread. The study concluded that it may be the aerodynamic effects of three-dimensional fire spread on the larger samples that lead to the observed change in behaviour in samples below 25mm, where flaming transitioned from laminar to turbulent. A summary of the results of different sample widths and the effects of heat release rate per unit width. $\frac{HRR}{w}$, as a function of pyrolysis height, x_p ,can be seen in Figure 3. The effect of sample width raises concerns regarding the validity of small-scale data when interpreted to determine the performance of a larger scale system such as an ORS. It also offers the potential benefits of an imposed external heat flux from cone heaters in order to compensate for the limited widths of samples. It was noted in liquid pool fire tests of n-decane, with a pool diameter of over 0.2m, that the impact of radiative heat transfer on rate of flame spread became significant relative to small diameter samples (MacKinven et al. (46)). Similar effects can be expected from larger samples of solid materials and the importance of radiative heat flux where the O_2 mass fraction is reduced has been shown in previous research discussed. The provision of irradiance in CACC testing offers an opportunity to explore the radiative effects of heat transfer of larger samples so long as the bench scale sample tested is of adequate size to expect similar aerodynamic effects acting upon the scaled down sample.

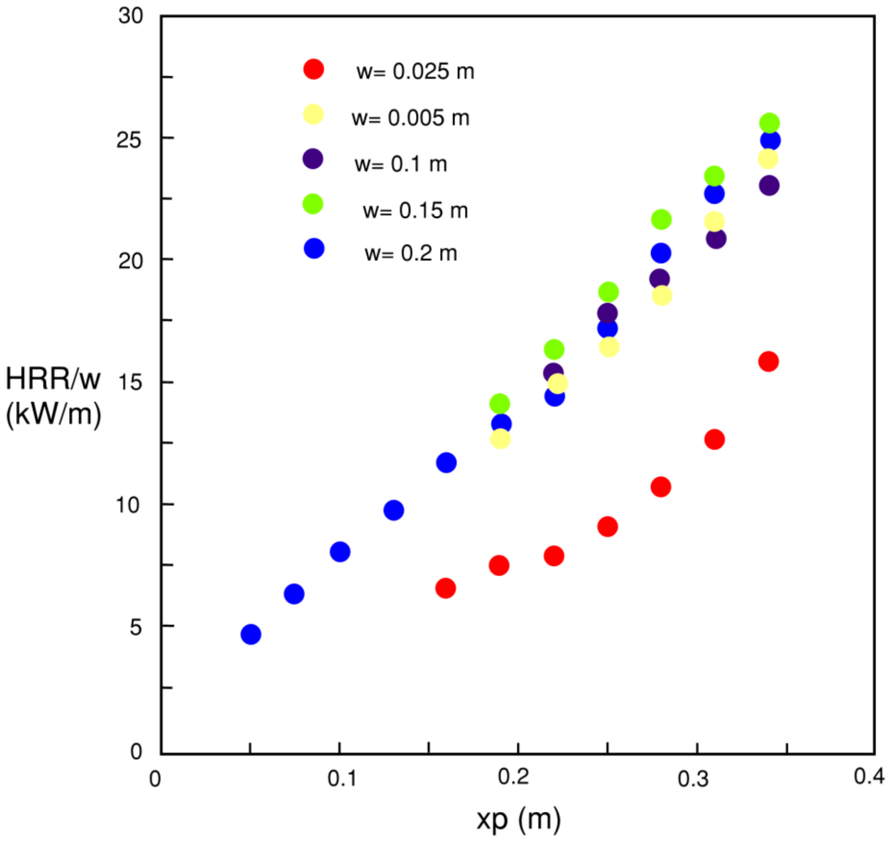


Figure 3 Heat release rate per unit width as a function of pyrolysis height at different sample widths (reproduced from Pizzo et al. (45))

Section 2.1.3 - A summary of the burning behaviour of ABS and general observations of burning polymers

The scope of the study conducted is primarily regarding the performance of polymers with particular focus on the burning behaviour of ABS. Numerous research papers on ABS have been reviewed in order to characterise its most noted burning behaviours as well as other properties that have been observed in the general decomposition of ABS. The general combustion process of polymers is via heat and mass transfer and involves complex chemical reactions as the application of heat promotes the interaction of free radicals with the products of sample gasification. The products of the condensed phase sample enter phase change and interact with other free radicals and oxidise via exothermic chemical reactions. The rate of decomposition of a sample is dependent on numerous factors including, as noted by Manohar et al (47), level of radiant heat flux, material surface reflectance and the absorption characteristics of the material. In particular, the absorption coefficient of a material dictates its ability to transfer the heat the material is exposed to at the surface into deeper layers of the material. If the absorption coefficient is low relative to the imposed heat flux then the surface of the material will heat rapidly to the point where decomposition will occur and mass transfer will take place as products of combustion are released.

One of the primary reasons for different behaviours observed in polymers when burnt is the method in which thermal degradation takes place as discussed by Kashiwagi (12). Kashiwagi notes that the majority of vinyl polymers degrade via free radical chain reactions. Initiated by thermal decomposition the addition of free radicals further increases the reactivity of the polymer chain causing chain scission which breaks the polymers chemical chain into smaller pieces. Many of the most common polymers are considered to thermally degrade in such a way, including PP, PE, PS and PMMA. Whilst the initial degradation by free radicals also occurs in other polymers, such as PMMA and polyoxymethylene, an additional reaction occurs yielding even smaller chemical chains and often monomer molecules Kashiwagi (12). Whilst the typical free radical chain reactions of samples yield very little charring this is no longer observed to be the case for samples including reactive side groups. Polymers containing these side groups cause the backbone of the polymer chain to degrade and ultimately lead to charring via polymer recombination as well as other potential reaction types. This is further supported by the work of Hietaniemi et al (48) who observed that the biggest predictor of variable behaviour of polymers in hypoxic conditions was whether the chemical compounds of polymers included chlorine or not. The inclusion of chlorine was found to radically change the burning rate in hypoxic conditions, propensity to ignite under certain applied heat fluxes and the yield of products produced from burning. The thermal degradation of ABS is caused by interaction with free radicals and occurs due to depolymerization (end chains), where a polymer chain breaks to form a new chain with low activity, and random scissions, where the backbone of the polymer chain is broken, as noted by Yang et al (13).

With the material burning behaviour of polymers so reliant on chemical chain reactions forming and breaking, a clear problem becomes apparent for material testing. This was noted by Morgan and Bundy (14) who performed numerous CC tests on multiple fire rated and non-fire rated polymers. They observed that HRR values were greatly dependant on the chemical structure of the samples tested. If the material behaviour is so reliant on its chemical composition how can a sample be shown to reliably represent polymer mixes? This is particularly the case for industries where composite polymers often have their base polymer ratios readjusted in order to provide optimal performance in certain fields of use. The problem becomes contextually more relevant as industries seek to optimise products through the varying use of polymer mixes. From the literary review conducted on fire research one point of note is the limited information journal articles often give on the material tested beyond the name of the polymer itself. Material name alone does not give any indication on the chemical structure of the polymer (Kashiwagi, (12)). Further information on base product ratios and discussion on chemical structure are rarely included within released works.

One of the largest material behaviour variables in burning polymers is the physical processes observed during material degradation. Some samples were observed to form bubbles, with finer, smaller bubbles observed when the applied external heat flux was increased, and melt (Kashiwagi, (12)). In other samples charring was observed (fire rated PP containing brominated fire-resistant material in Morgan and Bundy, (14)) whilst in other tests samples burned to completion with some slight expansion (PMMA in a CACC in Mulholland et al. (15)). In Kashiwagi and Ohlemiller's 1982 study(8) comparing PMMA to PE a molten surface layer was observed in both samples, at temperatures of approximately 120°C, causing dripping and sagging although the viscosity of the molten layer was much less for the PE sample than that of the PMMA. They also observed that bubbling in samples was less pronounced in higher heat fluxes, and that there was far less bubbling occurring in the PE sample. It was observed by Morgan and Bundy(14) that material behaviour presented challenges to researchers where trying to compare polymer data, for example, materials that charred, melt or intumesce were found unlikely to reach a steady state of HRR due to the constant fluctuation of material behaviour and physical properties throughout the test.

In a thermal degradation study on ABS, Tiganis et al. (49) found that the polybutadiene phase of ABS samples was the most critical to thermal degradation and that microcracks appeared in the degraded surface layer. Once the microcracks reached a surface layer depth of 0.08mm the cracks caused abrupt mechanical failure by propagating throughout the sample. It should be noted however, that the behaviour examined in the paper by Tiganis et al did not make use of bench scale test samples in a CC or FPA apparatus to examine behaviour under fire conditions. Rather, samples were exposed to heightened temperatures from 80°C to 120°C in oven conditions in accordance with ISO188 for up to 672 hours. The samples were then exposed to impact assessments in accordance with AS1146.1. Whilst the samples were not subjected to fire conditions the study does reveal an interesting point regarding the thermal degradation of polymers such as ABS; namely, it is the ratio of base polymers in ABS that will determine some aspects of burning behaviours and material properties. This conclusion is further reinforced by the findings of Yang et al(13) where ABS composites were combined with single walled carbon nanotubes (SWNTs). Whilst the study did not use a CC or FPA apparatus it did test samples up to 1000°C in a model 2960 TA instrument. The findings showed how complex composites can be with some of the samples, where the percentage of SWNTs was too high, destabilising the sample and causing it to degrade at lower temperatures whilst other samples, when SWNTs were included but at a much lower percentage, performed better than pure ABS.

Section 2.1.4 - Extinction theory of burning materials

As noted in Chapter 3 of 'Fire retardancy of polymeric materials', (Torero and Rein, (50)) extinction of flames is due to combustion reaction rates in the gas phase falling below a critical threshold. Once the reaction rate falls below this threshold the reaction no longer produces enough energy to allow self-sustained reaction. The energy balance in the gas phase of a burning polymer can be described as;

$$\dot{q}''_g = \Delta H_{C,F}\dot{m}''_{F,B} = \chi\Delta H_{C,F}\dot{m}''_{F,B} + \left(\dot{m}''_{F,B} + \dot{m}''_{O,B}\right)C_{pg}(T_F - T_\infty) + \dot{q}''_e$$

Equation 11

The reduction of flame temperature due to the production of negative values in Equation 11 will eventually extinguish flaming combustion. Whether extinction will or will not occur under certain conditions can be quantified by two non-dimensional numbers; the first and second Damköhler numbers. These numbers are defined as;

$$D_{a\mathrm{I}} = \frac{\tau_{Residence}}{\tau_{Conduction}} = \frac{reaction\,rate}{convective\ mass\ transport\ rate}$$

Equation 12

$$D_{a\mathrm{II}} = \frac{\tau_{Residence}}{\tau_{Chemical}} = \frac{reaction\,rate}{diffusive\ mass\ transfer\ rate}$$

Equation 13

The first Damköhler number represents the heat transfer, as shown in the denominator, against the heat necessary for the fuel to reach its ignition temperature locally, as shown in the numerator time as the residence time. These two timescales need to be such that heat losses from the sample as it cools are less than the convective heat transfer of the fuel. The second Damköhler number is more critical to the ORS principle as it represents the ratio of chemical reaction rate in the denominator to the necessary heat transfer rate for the fuel to reach its ignition temperature. When the oxygen concentration is altered locally the residency time in the numerator is reduced which decreases the second Damköhler number. If either of the Damköhler numbers are reduced below 1 then the fuel will be extinguished.

Fernandez-Pello et al (50) recognised the importance of oxygen mass fraction and opposed flow velocities on the Damköhler number and the subsequent correlation between low Damköhler numbers and a fuel burning rate leading to extinction. Fernandez-Pello et al (50) used a simplified expression to calculate the Damköhler number in certain conditions and to predict the nondimensional flame spread rate of PMMA samples;

$$D_{a\mathrm{II}} = C\frac{\mu_g p^n A_g Y_o (\ln(1+B)/B^{.15})}{Le\rho_g^2 U_m^2}$$

Equation 14

$$\cdot\, exp\left(-E_g/RT_f\right)$$

Where the Lewis number is defined as;

$$Le = \frac{\lambda_g}{\rho_g C_p D_g}$$

Equation 15

It should be noted however that the researchers concluded that the expression was not accurate enough to be used without further development as it was too sensitive to temperature and opposing flow velocity inputs. The resulting predicted activation energies of the reactions were found to be much too high compared to experimental data. However, it does highlight the relationship between the B number and the Damköhler number, i.e. the relationship between burning rate and extinction. Equation 14 also suggests the importance of the mass fraction of oxygen and the velocity of the opposing flow rate. In fact, flow rate velocity has a crucial role in the Damköhler number which changes depending on the oxygen mass fraction. For concentrations of O_2 above 30% an increased gas flow rate has been shown to increase flame propagation rates by increasing diffusion flame temperature and providing the force that repositions the diffusion flame behind the leading edge closer to the fuel. For concentrations of O_2 below 30% the opposite is true (Fernandez-Pello et al (50)), with flame propagation rates decreasing with increased opposing flow rate. This is because the cooling effect of the opposed flow will be found to dominate over the heating of the fuel by the flames. The reduced oxygen mass fraction lowers the flame temperature and convective heat losses from the flow are greater than convective heating from the flame. There is a balance between the interaction of fuel parameters, such as thermal thickness, flame parameters, and atmospheric parameters. Each of these parameters influence the residence time of the gas mixture as well as the chemical reaction time which in turn will influence the material burning behaviour observed in experiments. It is the importance of the Damköhler number at predicting material burning and extinction behaviour that has motivated some researchers to seek a method to measure it at different ignition conditions (gas velocities and oxidiser mass fractions) particularly since methods used to collect similar results from fuel mass flux results in large uncertainties (Delichatsios, (43)).

Section 2.1.5 - The use of hypoxic conditions to promote flame extinction

Hypoxic environmental conditions can be defined as conditions where the partial pressure of oxygen is lower than the partial pressure of oxygen as found at sea level. Hypoxic conditions can be found at high altitude although the environment in such areas differs from that of ORS systems as high altitudes are also classified as hypobaric whilst the environment in ORS are normbaric. The difference can be visualised as shown in Figure 4 and explains why the mass fraction of oxygen is reduced below ambient in normbaric hypoxic conditions.

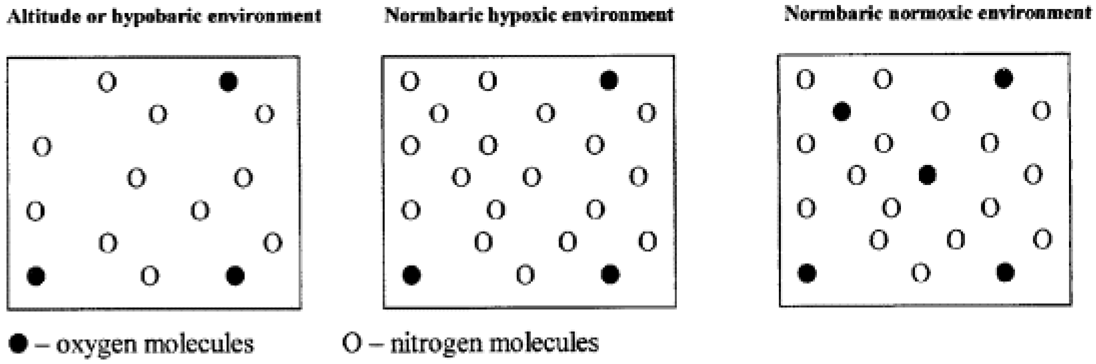


Figure 4 Difference between hypobaric and normbaric hypoxic environments (Kotliar (52))

From the discussions on the Damköhler number it can be discerned how the ratio of the reaction rate, with its necessary residency time, and the diffusive mass transfer rate can be altered by the changing composition of the atmospheric conditions. Changing the mass fraction of oxygen has two impacts on the Damköhler number as described in Equation 14. Firstly, in the numerator, the mass fraction of oxygen has an impact on the B number which concerns the burning rate of fuel as described in Equation 1. As the mass fraction of oxygen is reduced there is less available oxygen for the reaction process and therefore the reaction becomes more incomplete. As the combustion process deviates further from the ideal stoichiometric conditions the heat release rate lowers accordingly. As the heat release rate is reduced less preheating of the burning material occurs ahead of the flame front and the burning rate is reduced. This in turn reduces the heat release rate further. By lowering the oxygen mass fraction, it can therefore be expected that the reaction rate of the sample will be decreased which reduces the numerator of the Damköhler number. The mass fraction of oxygen also effects the denominator of the Damköhler number by the properties of the gas replacing the oxygen within the room. When the oxygen concentration is reduced the relevant properties of the replacement gas (specific heat capacity, density and thermal conductivity) are such that there is an increase in the characteristic chemical time. The increase in characteristic chemical time reduces the second Damköhler number and can eventually also promote extinction. The phenomena represented by the Damköhler number describes the two basic phenomena that limit ignition and fire growth in ORS systems, as noted by Barowy and Creighton (53). These are that in ORS systems there is less oxygen to promote combustion and that a greater amount of thermal energy lost due to the different properties of the replacement gas (typically nitrogen).

ORS systems are often assigned a limiting oxygen index/concentration (LOI/C) which describes the minimum percentage of oxygen within the local atmosphere that will support the combustion process of a solid material. As described in the material burning behaviour section of this literature review the LOC has an impact on the material burning properties which is in part due to the mode of heat transport (radiative or convective) that dominates at different oxygen concentrations. It is noted that the typical LOC applied to ORS, 15%, will not prevent the combustion of typical hydrocarbon materials (Xin and Khan (9)) and that the true extinction LOC may be much lower depending on the burning material and other local factors (local temperature, applied heat flux, orientation etc.). For example, Xin and Khan recorded a LOC for PMMA of 10.6% where the sample was horizontal and a 65kW/m^2 heat flux was applied. Whilst sample ignition has been shown to have a dependence on oxygen concentration its effect is limited and is typically only shown to have an impact at oxygen levels of below 14% (Babrauskas, (54)). Clearly then, ORS systems cannot be anticipated to prevent ignition in many fire scenarios. However, there have been reports of flame spread and speed being limited by reduced oxygen environments (Xin and Khan, (9)), (Tewarson and Ogden (42)) and (Rasbash and Langford (41)).

Whilst the reduction of oxygen concentration in ORS systems has a limiting effect on fire growth and development it can offer a limited impact on ignition and complete extinction for many fuels at 15% oxygen concentration. This is particularly the case for pyrolysis and smouldering combustion where the required oxygen concentration is lower, and the preheating zone of the material is sufficiently localised to generate enough energy to sustain burning. The work of Glassman (1977) defined two zones in diffusion flames, namely the reduction zone and the oxidation zone. As reported in Tewarson (10) the reduction zone is the point of interaction between the pyrolyzing fuel and the gaseous products created by the pyrolization. It is a fuel rich zone where some of the fuel is converted into products such as CO, soot and hydrocarbons. The extent of each product is difficult to predict as it is dependent on chemical variables originating from the fuels chemical structure as well as oxygen content of the surrounding atmosphere. In the oxidation zone products from the pyrolization process react with free radicals. This process involves the expenditure of O_2 and the generation of heat, CO_2 and H_2O. The effectiveness of ORS systems at 15% oxygen concentrations is in the flaming region (oxidation zone) and the prevention of rapid fire growth and not in the reduction zone as described by Glassman.

Literature Review Part 2 - Equipment Study

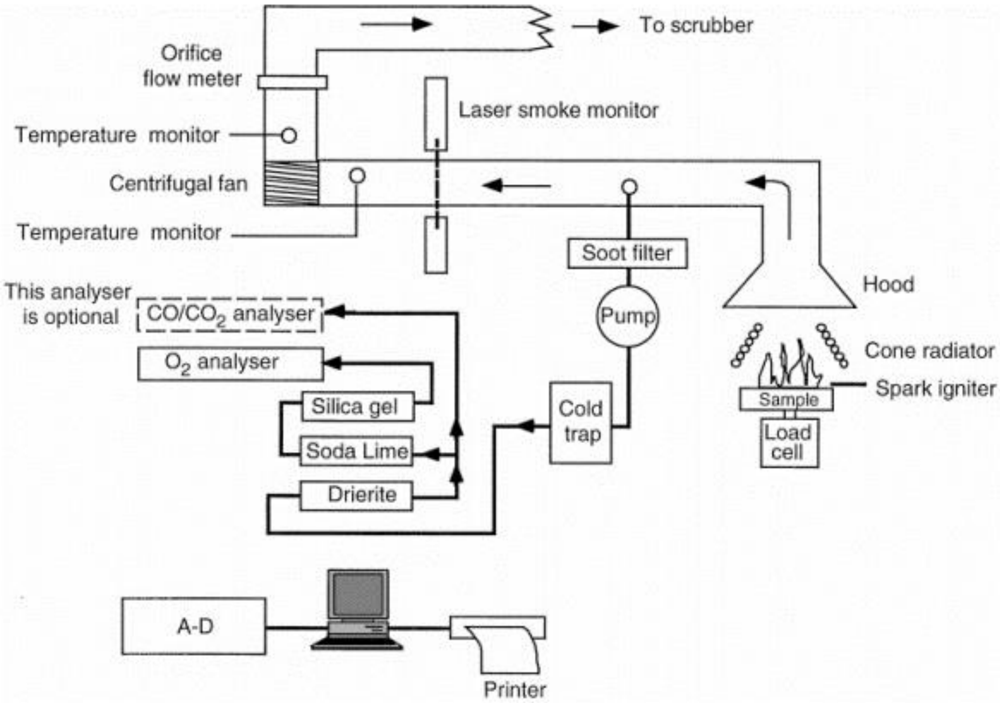
Section 2.2.1 - History and theory behind oxygen calorimetry

The impact of the cone calorimeter on the field of fire science is significant, in fact, it has been noted that oxygen consumption calorimetry has '*ushered in the modern era of fire safety science and engineering*' (Beyler, (56)). The fundamental principles from which the cone calorimeter is based upon, oxygen calorimetry, were discovered over 100 years ago (Thorton, (57)). Thorton recognised that many of the organic liquids and gases observed during testing consumed similar quantities per mass of oxygen for the net amount of heat that was released. It was not until decades later however that it was recognised that reliable measurements of heat release rate were a valuable and necessary tool for measurement in fire engineering (Emmons, (58)). Despite this, the measurement of heat release rate was not simple with the apparatus available at the time. Huggett (59) recounts that prior to the common application of CC, experiments were often conducted at room scale with the use of hundreds of sensors. The integration of the results of different sensors over the entire extent of full-scale experiments was challenging and vulnerable to measurement errors and inconsistencies. The need to develop a simpler and more reliable method of quantifying heat release rate spurred on research during the 1970's and 1980's.

Numerous studies recognised the correlation between heat release rate and oxygen depletion (Hinkley et al. (60)), (Christian and Waterman, (61)) but it was the work of Parker (62) and Huggett (63) that began to document heat release rate through oxygen consumption turning the work of Thorton from a conceptual observation to an empirically tested fact. In 1980 Huggett found that for most organic solids the average net amount of heat released per unit mass of oxygen was a constant value of 13.1 MJ$\cdot kg^{-1}$ and that this value was true with an error within $\pm 5\%$.

The development of a strong theoretical basis offered the opportunity to develop a more simplistic method of measuring heat release rate in samples on both a large and a small scale. After applying oxygen consumption calorimetry to a number of prototype designs, such as the NIST bench scale test method (Sensenig and Parker, (64)) the cone calorimeter was developed by Babrauskas et al. (65). Over the following years the research had been accepted by the regulatory community with the completion of the first cone calorimeter ASTM standard (1990) (66) and ISO standard (1993).

Studies testing material properties at vitiated oxygen conditions clearly cannot be conducted within a CC owing to its open design. Prior to the common use of the CC experiments, in hypoxic conditions were often conducted in FMRC Flammability Apparatus (Tewarson et al. (10) (24)). However, many different designs for a controlled atmosphere cone calorimeter were being proposed by the 1990's and 2000's (Babrauskas and Mulholland, (67)), (Petrella and Christy, (68)) and (Leonard, (69)). It was the intent of CACC designs to maintain the operating capabilities and usability of a typical CC whilst being capable of operating at oxygen conditions of between 0% and 20.95% in flow conditions similar to those observed in standard CC tests. As listed by Leonard (69) the main differences between a typical CC and a CACC include the introduction of a flow of nitrogen mixed with air to lower the mass fraction of oxygen and the introduction of an air diffusion bed to ensure that the flow of the N_2/air mixture does not disrupt the flaming combustion of the sample. For some CACC system designs there is also a repositioning of system ductwork and fans to allow the 'blowing through' of combustion products rather than the 'sucking up' of such products as used in a typical CC. A schematic comparing the design alterations of a CACC, as used by Werrel (70), where compared to a typical CC design can be seen in Figure 5.



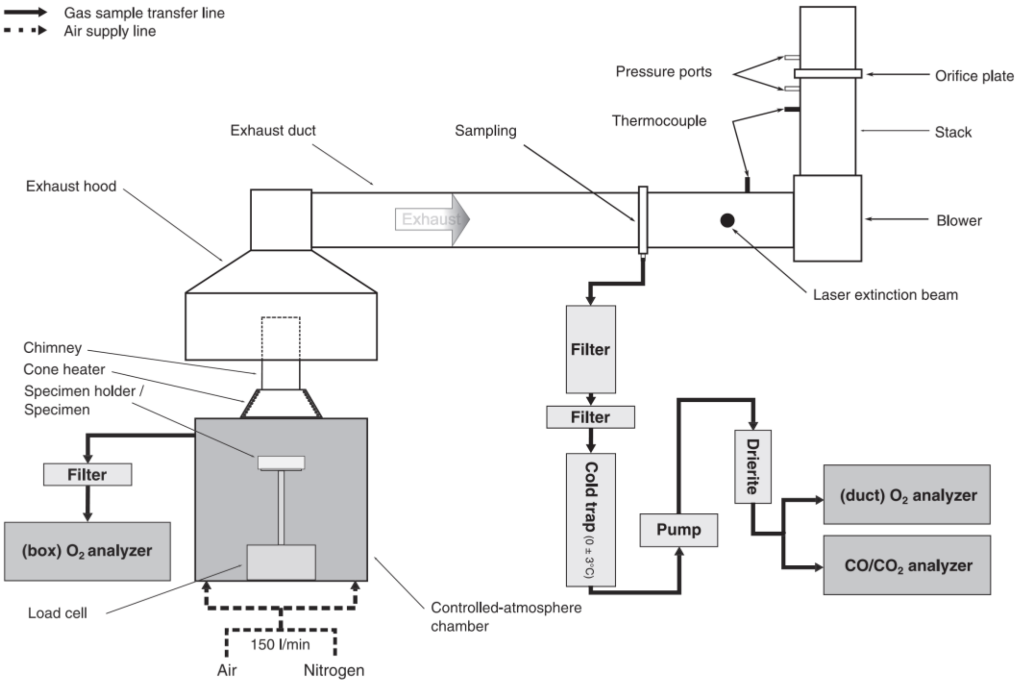


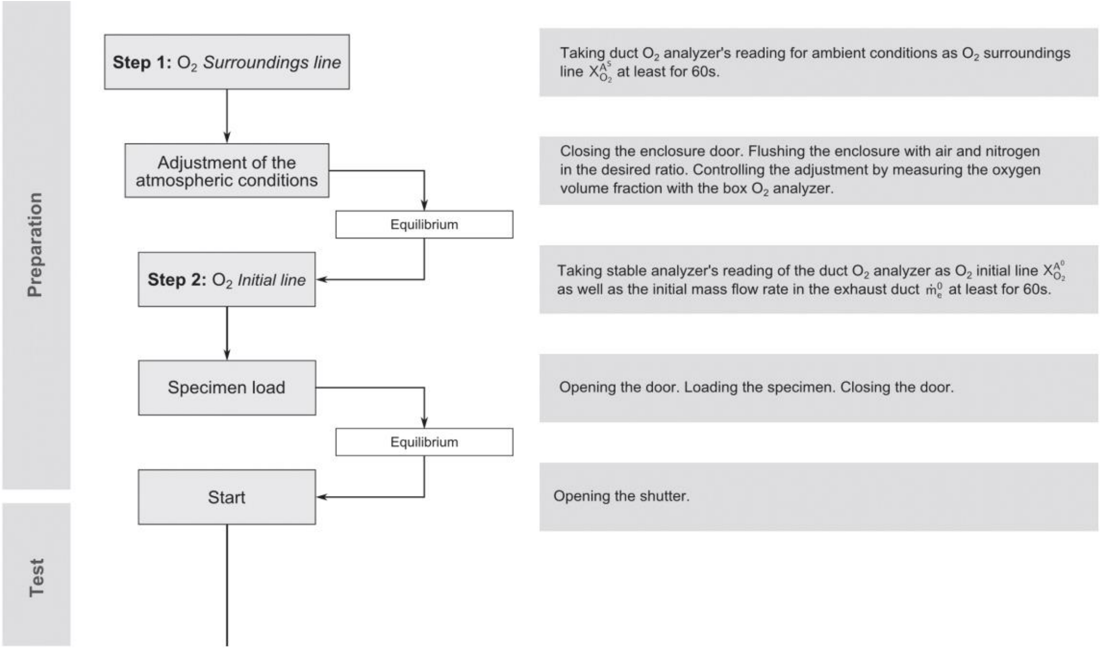
Figure 5 Schematic of CC (top) (Leonard (69)) and CACC (bottom) (Werrel et al, (70))

Section 2.2.2 - General procedure and differences between CC and CACC apparatus

In accordance with ISO5660-1:2015 the procedure for cone calorimetry in ambient conditions involves preparing a sample of approximately 100mm by 100mm, with a width of between 1-50mm, exposing the sample to a radiant heat source ranging from 0-100kW/m^2 and then applying ignition, usually via a spark igniter, to the sample. The sample is secured in position using a sample holder and is located underneath an exhaust duct and on top of a load cell which periodically measures the samples weight. To prevent the premature heating of the sample a radiation shield is used to limit exposure to the cone heater until the test begins. The exhaust duct above the sample removes the incomplete combustion products from the vicinity of the sample and takes measurements of the sample's oxygen consumption. There is also a laser within the exhaust ductwork which measures the obscuration caused by smoke produced during the test.

The modified procedure for the CACC is as described by Werrel (70) and deviates from the ISO standard for cone calorimetry. Evident differences between CACC and CC apparatus are observed even before comparing the procedures of each. There are differences in schematising the operating process, as described by Leonard (69) and shown in Figure 5. There are also differences in the apparatus used, i.e the enclosure of the sample in a controlled atmosphere chamber fed with a controlled flow of N_2 and air as well as a chimney connecting the controlled atmosphere chamber to the exhaust hood. There are even differences between available CACC apparatus with 'open' (where there is an open connection between the chamber and exhaust hood) and 'closed' (where there is no open connection between the chamber and the exhaust hood) variants. The installed equipment in Lund University is as per the 'open' CACC design and therefore the apparatus arrangement and procedure for this design have been discussed further.

The procedural alterations for the CACC all concern the preparation and calibration of the equipment to determine an O_2 reading prior to inserting the sample. The ambient conditions are collected with the O_2 analyser for 60 seconds as per ISO5660-1:2015(71) but then the chamber door is closed, and the chamber is flushed with air and nitrogen (ratios as per desired tested conditions and calculated as discussed in Section 3). Once the closed chamber has been flushed with the N_2/air mixture and has reached equilibrium at the correct ratio, a new O_2 reading is taken for 60 seconds as well as the mass flow rate of the gases introduced into the inlet. Following this, the door to the chamber is opened and the sample is introduced. Once introduced, the door of the chamber is closed, and equilibrium is reintroduced into the chamber as soon as possible to avoid pre-heating the sample (this process was measured prior to testing at 45 seconds as described in Section 3). The mole fraction of O_2 is measured by the oxygen analyser for the remainder of the test as it is assumed to be variable in the HRR calculation for CACC rather than the constant assumed in the HRR calculation of the CC found in ISO5660-1:2015. A general summary of the procedural differences as given in Werrel (70) is shown in Figure 6.



Taking duct O_2 analyzer's reading for ambient conditions as O_2 surroundings line $X_{O_2}^{A^S}$ at least for 60s.

Closing the enclosure door. Flushing the enclosure with air and nitrogen in the desired ratio. Controlling the adjustment by measuring the oxygen volume fraction with the box O_2 analyzer.

Taking stable analyzer's reading of the duct O_2 analyzer as O_2 initial line $X_{O_2}^{A^0}$ as well as the initial mass flow rate in the exhaust duct $\dot{m}_e^0$ at least for 60s.

Opening the door. Loading the specimen. Closing the door.

Opening the shutter.

Figure 6 CACC procedural changes from ISO5660-1 (Werrel, (70))

Section 2.2.3 - General heat release rate (HRR) calculation and changes for CACC procedure

As well as the procedural changes between the typical cone calorimeter method in ambient conditions and the controlled atmosphere cone calorimeter in hypoxic conditions the calculation of heat release rate is also revised. The heat release rate equation as per ISO5660-1:2015 is shown in Equation 16.

$$\dot{q}(t) = (\Delta h_c / r_o)(1.10)C\sqrt{\frac{\Delta p}{T_e}} \cdot \frac{X_{O_2}^0 - X_{O_2}}{1.105 - 1.5X_{O_2}} \qquad \text{Equation 16}$$

Where;

$$X_{O_2}(t) = X_{O_2}^1(t + t_d) \qquad \text{Equation 17}$$

The equations given within ISO5660-1:2003 are a simplification of the original equations proposed by Parker (72) but revised by Janssens (73) to a per unit mass of O_2 rather than the original per unit volume given by Parker. The ISO equations have been simplified such that values for the mole fraction of CO_2, CO and H_2O are not required and that easily measurable quantities can be used to calculate heat release rate. The reason for this is partially economic due to the additional cost of chemical scrubbing agent needed to measure the mole fraction of the gases within the exhaust duct (ISO5660-1:2003). The equation from which the ISO standard is based upon is the oxygen mass consumption equations for heat release rate per unit mass as proposed by Janssens (73) in Equation 18.

$$\dot{q} = \left[E\phi - (E_{CO} - E)\frac{1-\phi}{2}\frac{X_{CO}^{A}}{X_{O_2}^{A}}\right]\frac{\dot{m}_e}{1+\phi(\alpha-1)}\frac{M_{O_2}}{M_a}\left(1 - X_{H_2o}^{0}\right)X_{O_2}^{A^0} \qquad \text{Equation 18}$$

Where the oxygen depletion factor is calculated as;

$$\phi = \frac{X_{O_2}^{A^0}\left(1 - X_{CO_2}^{A} - X_{CO}^{A}\right) - X_{O_2}^{A}\left(1 - X_{CO_2}^{A^0}\right)}{\left(1 - X_{O_2}^{A} - X_{CO_2}^{A} - X_{CO}^{A}\right)X_{O_2}^{A^0}} \qquad \text{Equation 19}$$

The mole fraction of oxygen in incoming air, $X_{O_2}^{A^0}$, is not measured throughout typical cone calorimetry because of the limited number of gas sampling points on the apparatus. Instead, the baseline oxygen analysis measurement taken during the initial 60 seconds of the test is used as the mole fraction of the incoming air. The value is considered constant for the remainder of the test in the CC. The conventional baseline approach described is reasonable in a CC because the sample is not enclosed and therefore ambient air is available to the combustion process at a constant rate. The baseline value is a reasonable approximation of the mole fraction of incoming air which is not influenced by the duct mass flow rate.

In an open CACC system the assumption of a constant mole fraction of incoming oxygen is no longer reasonable due to the partial flows from the chimney of the enclosed chamber and the ambient air entering the flow of gases travelling between the chamber and the exhaust hood. The reason for the combined flow, of enclosed chamber volatiles and excess air from the surroundings, is due to the disparity between flow leaving the chamber and the extract fan in the ductwork. The ductwork will always have a greater mass flow and therefore excess air from the surroundings will be drawn in to satisfy the system balance. As the extract system in the exhaust ductwork is controlled by a fan, typically running at a flow rate of 24l/s, the volumetric flow rate is constant whilst the changing heat within the chamber is changing the mass flow in the ductwork. The mixed supply of N_2 and air entering into the chamber is also forced for CACC apparatus and has both a constant volumetric flow rate as well as a constant mass flow rate. This is because as gases entering the chamber via the N_2 and air cylinders do not interact with the heated sample prior to entering into the chamber. It is the dynamic influence that the flaming sample has on the mass flow through the exhaust duct, due to heat differentials, when coupled with the constant mass flow into the chamber, from the N_2 and air cylinders, that causes the flow ratio between the mass flow from the chamber and the mass flow from the laboratory surroundings to vary in time. For this reason, the conventional baseline approach, where a 60s range of O_2 mole fractions in incoming air is taken as a constant value over the extent of the test, is not reasonable in the CACC calculation procedure.

The problem identifies an incompatibility between the calculation procedure of CC and the apparatus in CACC. Therefore Werrel (70) identifies a revision to the calculation procedure which results in the following equations to calculate heat release rate. The heat release rate equation is modified as shown in Equation 20.

$$\begin{aligned}\dot{q} = E \cdot 1.10 \cdot \left(X_{O_2}^{A^0}\gamma - X_{O_2}^{A^S}(\gamma - 1)\right) \\ \cdot C\sqrt{\frac{\Delta p}{T_e}}\left[\frac{\phi - 0.172(1-\phi)X_{CO}^{A}/X_{O_2}^{A}}{(1-\phi) + \phi\left(1 + 0.5\left(X_{O_2}^{A^0}\gamma - X_{0_2}^{A^S}(\gamma - 1)\right)\right)}\right]\left(1 - X_{H_2O}^{S}\tilde{\gamma}\right)\end{aligned} \qquad \text{Equation 20}$$

With the oxygen depletion factor in this case defined as;

$$\phi = \frac{\left[\left(X_{O_2}^{A^0}\gamma - X_{O_2}^{A^S}(\gamma - 1)\right)\left(1 - X_{CO_2}^{A} - X_{CO}^{A}\right)\right] - \left[X_{O_2}^{A}\left(1 - X_{CO_2}^{A^S}\tilde{\gamma}\right)\right]}{\left(1 - X_{O_2}^{A} - X_{CO_2}^{A} - X_{CO}^{A}\right)\left(X_{O_2}^{A^0}\gamma - X_{O_2}^{A^S}(\gamma - 1)\right)}$$

Equation 21

Where;

1.10 – ratio of molecular weights of oxygen and air

0.172 – ratio of net heat releases per oxygen mass consumed

0.5 – chemical dilution

It can be noted in Equation 21 that the value that had been '$X_{O_2}^{A^0}$', the measured mole fraction of oxygen in the incoming air, in Equation 19 has been replace by the term $\left(X_{O_2}^{A^0}\gamma - X_{O_2}^{A^S}(\gamma - 1)\right)$. Werrel refers to this term as the readjusted mole fraction of O_2 in incoming air during the test as defined in Equation 22.

$$X_{O_2}^{A^{in}} = X_{O_2}^{A^0}\gamma - X_{O_2}^{A^S}(\gamma - 1)$$

Equation 22

The gamma term is defined as the thermal expansion factor and is a time dependant ratio of two measured quantities taken during the test procedure. The $\dot{m}_e^0$ represents the mass flow rate in the exhaust duct prior to the test and is the initial value taken during the 60 seconds where the correct flow of N_2/air has been introduced and reached equilibrium. The m_e represents mass flow rate in the exhaust duct during the test. This value is time dependant as noted in the procedural discussion for the CC and CACC.

$$\gamma = \frac{\dot{m}_e^0}{\dot{m}_e}$$

Equation 23

It should also be noted that the value for $X_{CO_2}^{A^0}$, representing the measured mole fraction of carbon dioxide in the incoming air, has also been replaced between Equation 19 and Equation 21. The value has been replaced by the term $X_{CO_2}^{A^S}\tilde{\gamma}$. This has been replaced following the same principle as the changes for O_2 shown in Equation 22 and Equation 23 where a constant term in the oxygen depletion factor has been replaced with a time dependant variable reliant on the measured mole fraction of CO_2 in the surrounding air, term $X_{CO_2}^{A^S}$, as well as a thermal time varying factor named the dilution factor, $\tilde{\gamma}$, which is given in Equation 24. The term $\dot{m}_g^B$ represents the mass flow rate of the incoming gas mixture to the enclosed box and is a time dependant variable.

$$\tilde{\gamma} = 1 - \frac{\dot{m}_g^B}{\dot{m}_e}$$

Equation 24

Equation 20 and Equation 18 also include numerous alterations from the typical model as given by Janssens (73) and the CACC adapted version as given by Werrell (70). Due to the limited scope for the current project the full calculation procedure will not be given, however, it can be noted that the mole fraction of H_20 in the surrounding air is also made variable in time with the inclusion of the dilution factor term. Finally, because the $\dot{m}_e$ term, the mass flow rate of incoming air, is not a known term, it has calculated instead using Bernoulli's Law at an orifice plate in the exhaust duct as shown in Equation 25.

$$\dot{m}_e = C\sqrt{\frac{\Delta p}{T_e}} \qquad \text{Equation 25}$$

Section 2.2.4 - Discussion of equipment uncertainty and unknowns

It has already been noted that cone calorimetry has an uncertainty of $\pm 5\%$. This is due to the variable degree of truth to the assumption upon which oxygen consumption calorimetry is based for different organic solids. This assumption, that for every unit mass of oxygen consumed there is a net amount of heat released of 13.1 MJ· kg^{-1}, will depend on the fuel but the attributed error that this deviation introduces has been considered acceptable for the calculation of heat release rate.

However, as well as the uncertainty introduced through the general assumption made in oxygen calorimetry there have been numerous studies on other potential inconsistencies introduced by the approach. Schartel et al. (21) notes that cone calorimetry is often used as a universal approach to ranking and comparing materials. This is however sometimes difficult due to the variable material behaviours and heat release rates which are more dependent on user inputs, and experimental setup then sometimes acknowledged. Schartel et al make particular reference to the importance of imposed heat flux and how a large level of uncertainty is introduced when attempting to predict material behaviour at a heat flux different from that tested. It is noted that using higher heat fluxes has the advantage of reducing the uncertainty, create more reproducible results and can reveal telling differences in material behaviour more readily. The heat flux applied is an important variable because it replicates the fire scenario that the material is predicted to be exposed to and the conceptual material burning behaviour may be altered. Where the altered material burning behaviour, is related to the fire retardancy of the product this can have significant outcomes. Bartholmai et al. (39) reported that, on comparable samples of layered silicate PP-g-MA nanocomposites where the exposed irradiance was varied between 35-70kW/m^2, the peak heat release rate varied by between 40% and 80%.

Schartel et al (21) also notes the importance of the distance between the cone heater and the sample and how variations of distance during testing, from intumescent expansion or deformation by melting, can impact result replicability and comparison with other data. The change of distance to the cone heater is considered by Schartel to only be a problem where there are 'extreme' changes in horizontal or vertical distances of samples during testing with external heat fluxes being relatively insensitive over deformation distances in intumescence systems of up to 3.5cm.

Schartel also noted the importance of the sample holder to collected results, with the insulation of the sample holder having a significant impact on the peak heat release rates observed in samples. This research is further supported by the comments of de Ris and Khan (74) who noted that flammability measurements were apparatus dependant without such heat losses from sample holders being quantified in testing. The comments made by de Ris and Khan were noted to be especially true for thermally thin samples and low heat fluxes where, in both cases, sample holder design and preparation was deemed to have a large effect on measured properties. Albeit for an FPA apparatus, de Ris and Khan proposed a new sample holder which reduced heat losses and therefore reduced the apparatus influence on experiment result variability due to sample preparation.

Further uncertainty is discussed by Marquis et al (75) regarding the comparison of results collected from different CACC procedures and apparatus. Within the study it is noted that the height of the chimney on top of the combustion chamber alters the performance of the CACC as shorter chimneys will increase the post oxidation phenomenon discussed previously by Werrel. The optimum height, as discussed by Marquis et al, is 0.6m and has been used in the Lund University laboratory set up. Marquis et al also noted the importance of inlet airflow into the enclosed chamber of the CACC and found that if the airflow was too low then there would be an accumulation of fuel gases within the chamber. The accumulation of fuel gases would reduce the mass fraction of 0_2 in the controlled environment to below the intended oxygen concentration desired from the inflow of N_2 and air thereby having an influence on the material burning behaviour. It was found by Marquis et al (75) that an air flow rate of $160l.min^{-1}$ would sufficiently promote flow within the chamber to ensure that the correct conditions were maintained and that material behaviour would not be inadvertently influenced by the apparatus operating conditions.

An earlier study by Marquis et al (76) provides evidence, collected from repeat experiments using 4 different variations of CC and CACC setups, that in ambient conditions the design of the CC and CACC does not substantially change the experimental results although there is evidence of some variation at higher heat fluxes. This variation, as seen in Figure 7, is explained by Marquis as likely due to the radiative feedback from the heated chamber of the CACC acting upon the tested sample. The chamber chimney in this instance would also have some influence on the oxidation of the gas species as the sample thermally decomposes. These effects were shown to affect the measurement of HRR much more than the HOC and MLR as shown. The influence of apparatus design in hypoxic conditions from the same study is also shown in Figure 8. It can be seen that there is significant result variation particularly at lower O_2 percentages and that the use of the correctly sized chimney (0.6m) becomes integral to minimising the influence of apparatus design on collected results. On the basis of these findings a CC was used for ambient tests (to limit the uncertainty in Figure 7) and a CACC with a chimney was used in hypoxic tests (to limit the uncertainty noted in Figure 8).

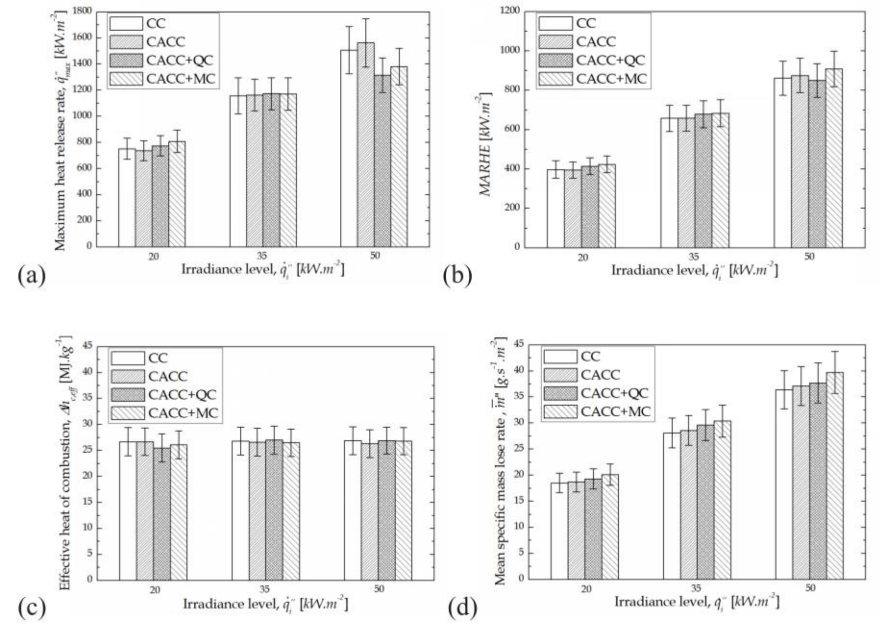


Figure 7 Repeat tests measuring uncertainty between apparatus setup in ambient conditions (Marquis, (75))

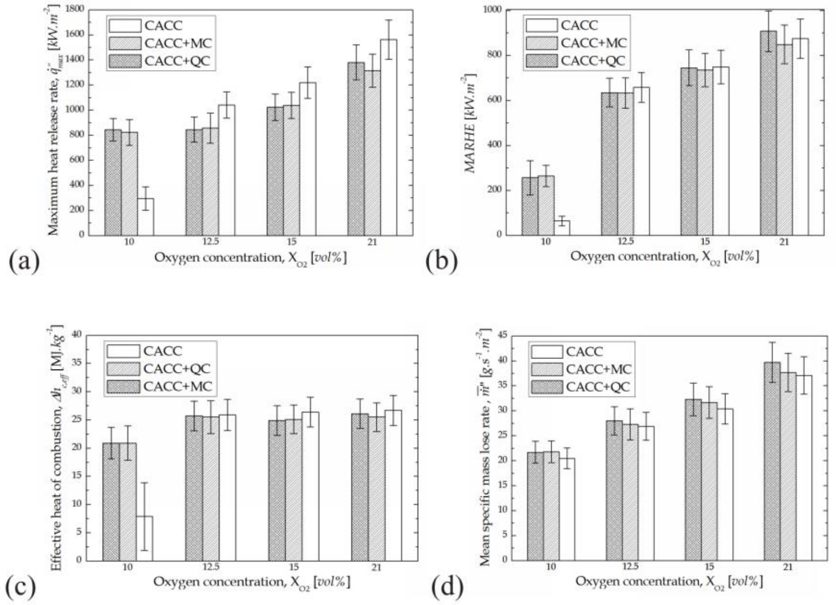


Figure 8 Repeat tests measuring uncertainty between apparatus setup in hypoxic conditions (Marquis, 2013)

It should be noted that Figure 8 experiments were performed with an irradiance of 50kW/m^2, the bars are weighted averages of three repeat tests and that QC = quartz chimney and MC = metal chimney. MARHE = Maximum average rate of heat emission.

It has been discussed that it is not simply the intrinsic uncertainty of the cone calorimetry equipment that influences the results collected but also the user inputs and apparatus used. Uncertainty has been limited as discussed in Section 3 which notes the methodology used within the experiments conducted and how uncertainty has been mitigated against. Despite this, it is recognised that uncertainty cannot be entirely removed from the study conducted.

Literature Review Part 3 - ORS Regulatory Standard Literature Review

The following section briefly summarises two regulatory standards that were reviewed for the purpose of the work undertaken. EN16750:2017(79) and VdS3527:2018(77) both concern the use of ORS as a method of fire prevention rather than suppression. Both documents explicitly state that ORS design in accordance with the guidance followed aims to limit fire ignition and reduce fire spread and not to ensure fire extinguishment. Both regulatory standards make use of the inert gas nitrogen as the method of reducing the mass fraction of oxygen within the protected compartment of the ORS.

It should be noted that EN16750:2017(79) contains specific mention of the inability of ORS designs to adequately prevent smouldering processes such as overheated cables and that such risks must be protected by other means. VdS3527:2018(77) makes no such mention of this burning behaviour and the limitations of ORS in this regard. Both documents refer to materials that are inappropriate for inclusion within ORS compartments such as chemicals which release oxygen when burning, chemicals that undergo auto-thermal decomposition and highly reactive metals.

Both documents acknowledge the necessary considerations to burning behaviour within the system design. Both mention the following (within Section 5.8 of VdS3527:2018(77) and Section 5.4 of EN16750:2017(79));

- Combustible material itself
- Geometry of the material
- Temperature and pressure of the protected zone
- The gas volume within the enclosed combustible materials (for example if the sample has an enclosed, hollow body or is formed of densely packed storage goods)

VdS3527:2018(77) makes additional mention of the importance of the type of ignition source itself, its ignition energy and the overall design aim of the system. The inclusion of the volume of gas stored within the combustible material is of particular interest to the current study which aims to test composite materials featuring pockets of air at ambient concentrations of oxygen.

It is noted that both regulatory standards place the onus of determining the design parameters on the designer. Whilst factors necessary to the determination of a suitable system design are made it is the designer's responsibility to ensure that the effective form and geometry of the material stored within the ORS is adequately covered within the system design. In Section 1.5 of VdS3527:2018(77) and Section 5.5 of EN16750:2017(79) the standards advise the ignition threshold for the system design should be based on the lowest ignition threshold of the materials within the ORS and that the geometry should be factored into this decision. However, neither standard gives a quantifiable method for considering geometry, orientation or composite samples without testing and only provides the designer with data on pure materials for design purposes (Annex B in VdS3527:2018(77) and Annex A in EN16750:2017(79)).

In order to account for the approximate nature of the design methodology for ORS both standards apply a safety margin to the ignition threshold. For VdS3527:2018(77) this is set to 1.0% by oxygen volume which can be increased in cases where the oxygen monitoring device is less accurate or local variations in nitrogen concentration are prone to fluctuation. EN16750:2017(79) applies a 0.75% by volume oxygen concentration safety margin to the ignition threshold but also provides a method of calculating a lower ignition threshold which factors in the oxygen monitoring device, the range of nitrogen fluctuations and risk classification of the system.

Both standards give the ignition threshold (% by volume of oxygen) of ABS as 16% which is reduced to 15.9% when the ABS component involves an IT risk. Packaging foil (such as bubble wrap) has an ignition threshold of 15.9% and cardboard has an ignition threshold of 15% in both standards. All ignition thresholds need then to be applied with the relevant safety margin as previously discussed.

Both standards also present designers with a method of determining the required oxygen concentration by way of a full room test (Annex E of VdS3527:2018(77) and Annex A.2 of EN16750:2017(79)). The EN16750:2017(79) test involves a compartment not smaller than 100m^3, which can be reduced to not less than 10m^3 if the two lowermost oxygen sensors have an accuracy that does not deviate more than 0.1% during the test. Within the room test specimens of at least 25mm by 200mm, and with a thickness not greater than 25mm, are placed on a support or hung in a vertical position. The sample must be a minimum of 1000mm off of the floor of the test room. An oxyacetylene torch is applied to the specimen at an angle of 90° towards a lateral side of the specimen with the flame outlet 200mm away from it. The flame, which has a temperature of between 900°C to 1000°C and a length of 300mm, is applied to the sample for 3 minutes. If the sample burns independently or flame spread is observed, after a minute from when the flame is removed, then the sample has failed the test and the oxygen concentration must be reduced further. The test is repeated twice more to ensure validity.

The VdS3527:2018(77) test involves a test room with a volume more than 10m^3 and minimum dimensions in all directions of 2m. Samples are of a similar size to EN16750:2017(79) at 25mm by 5mm by 200mm. The thickness in this case is not greater than 25mm. The sample is installed in the middle of the room test at a height of 1000mm and is ignited using an oxyacetylene burner. The burner flame needs to be at least 1000°C and has a length of 150mm ±20mm. The flame is applied to the bottom edge of the test sample and will be traced vertically, at a distance of approximately 100mm, should the material begin to be consumed or deformed. The angle of the flame is approximately 45° during this process and the sample is exposed to the flame for 3 minutes. Where the sample is still burning a minute after the removal of the flame the test has failed, should the sample be reignited by molten droplets the test is also considered to have failed. Should the test sample fail the oxygen percentage volume is reduced by 0.5% and a new sample is tested. As with EN16750:2017(79) the test is carried out three successive times to ensure validity.

From reviewing the room test procedures proposed by the two standards the primary differences can be found in the ignition source. This is particularly true when considering the dimension, length and position of the flame itself. It is noted that neither standard imposes a heat flux to the sample, both samples are located in the centre of the test room (rather than the corner where more radiant feedback to the sample would be anticipated) and that the test is conducted without the inclusion of other adjacent samples stacked horizontally and vertically.

The current design standards do not contain detailed quantifiable data on composite materials and the impact of sample orientation and ORS contents geometry on the ignition threshold for the system design. There is also conflict regarding the most suitable method of applying ignition sources to tested samples. This reflects the effect that a lack of research data into the material burning behaviour has had on the real-world design of ORS protection with highly approximated safety margins applied in lieu of research based design. The conclusions are further supported by the work of Nilsson and van Hees (80) who, in their review of test standards PAS 95:2011(78) and VdS3527(77), noted that the ignition source was unsuitable for the proposed application due to its high burning velocity (causing blowout of diffusion flames on the sample), the location of the fuel does not consider radiation effects of neighbouring obstructions and that the sample within the test method does not consider fuel configuration as would be expected. Subsequently, there is a clear motivation to supplement further research in the field of hypoxic burning behaviour in order to progress the room testing methods of regulatory standards as well as the general design recommendations for ignition threshold of materials.

Section 3 - Methodology

Quantitative methods of data collection and analysis were used to satisfy the research goals. This included the use of a cone calorimeter (CC) and a controlled atmosphere cone calorimeter (CACC) used to collect the oxygen calorimetry data of numerous burning samples. The following section outlines an overview of the equipment and procedure used.

Section 3.1 - Cone calorimeter calibrations prior to testing

It was imperative that the CC/CACC was correctly calibrated before testing with checks described in ISO5660-1:2015 for the irradiance control system, the weighing device, the oxygen analyser, as well as other components of the gas analysis system. Adherence to CC calibration procedure, as per ISO5660-1:2015, was followed during the experiments conducted. The calibration process ensured that the correct zero and span values for the full range of O_2, CO_2 and CO were fully captured. Zero and span values were also collected for the laser collecting smoke obscuration data. The C factor, which accounts for flow properties through the ductwork, was also calibrated on a daily basis using a methane burner inserted under the hood at a flow rate achieving 5kW. The range of acceptable C factor values was in accordance with the range of values given by Fire Testing Technology Ltd. Adherence to CC calibration procedure, as per ISO5660-1:2015, was followed during the experiments conducted. The balston filter was changed daily or whenever the sample pump flow was reduced below the desired values due to a blockage within the filter. The flow rate was checked regularly, and no blockages occurred during testing such that the flow dropped to an unacceptable value.

In accordance with the ISO5660-1:2015 standard, immediately prior to testing, final checks were conducted on the CO_2 and moisture traps, with the sorbent within these traps being replaced where necessary. Temperature checks on the trap ensured that it did not exceed 4°C. The distance between the cone heater and the base plate was adjusted to limit the variability of heat flux exposure between different samples. The exhaust fans were set to a flow rate of (0.024 ± 0.002) m^3/s.

Section 3.2 - Laboratory equipment

Both a cone calorimeter and a controlled atmosphere cone calorimeter were used during the experiments. Section 2 Part 2 contains detailed discussion regarding the calculation procedure and general uncertainties of the equipment used. The CC/CACC installed within the Lund University laboratory was first installed by ‘Fire Testing Technology Ltd.’ On 19/06/14 and is installed as shown in Figure 9.

Figure 9 CC apparatus (left) and CACC installation (right) at Lund University

As previously discussed, cone calorimetry is a well-established and frequently used research method for measuring the variables considered within the experiments conducted. Whilst undertaking testing in hypoxic conditions does somewhat deviate from the typical procedures for the cone calorimeter, as found in ISO5660:2015, its validity has been well documented in the work of Werrel(70). The equipment is therefore suitable for measuring the target variables monitored within this work, and subsequently, will achieve the research objectives of the work. The use of nitrogen as the inerting gas in the chamber is considered reasonable due to its common use in ORS as the replacement gas to reduce the oxygen mass fraction.

Despite the limitations and weaknesses of cone calorimetry, as described in Section 2 Part 2, the equipment is considered to be the most appropriate for the experiments conducted. In part, this is due to the need for test data that is replicable and applicable to the work of others. Using an established and widely used test apparatus ensures that this desire is met.

Prior to conducting experiments, a risk assessment was performed on the laboratory equipment and the materials tested, found in Section 9, which ensured that the safety of those working within the laboratory was considered during testing. These ethical considerations helped to maintain a safe working environment for those involved as well as the wider Lund university community.

Section 3.3 - Sample materials

One of the primary objectives of the work conducted was to collect and analyse material combinations that had not been widely tested, in the experimental literature reviewed, under hypoxic conditions. This involved testing composite samples of varying thicknesses. Additionally, bubble wrap was used to introduce a small number of aerated pockets into the test samples. The following sample materials were burnt during the tests;

- ABS (Acrylonitrile Butadiene Styrene)
- Cardboard
- Bubble wrap

26 pure ABS samples were tested at varying thicknesses, 5mm, 10mm and 20mm, and densities. 26 composite samples were also tested with the same ABS thicknesses but with an additional top layer of approximately 5mm cardboard and 10mm polythene bubble wrap. The cardboard and bubble wrap layers represent a typical composite arrangement for material storage within ORS compartments. Figure 10 illustrates the pure and composite samples at the varying thicknesses tested.

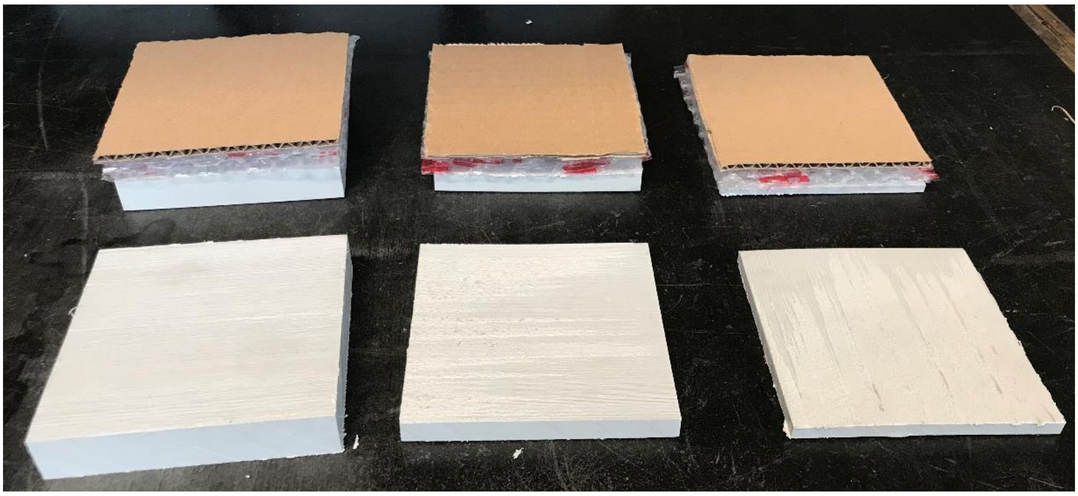


Figure 10 Thicknesses of pure ABS and composite samples

It is noted that the sample materials do not necessarily represent permitted contents of ORS systems as the standards note that designers should be aware of the inclusion of layers which could contain pockets of ambient air concentrations. However, it is not the intent of this thesis to directly test samples as per the ORS standards reviewed. The thesis aims to identify and review contributory factors for material behaviour under hypoxic conditions. A bubble wrap layer has been chosen due to the limited amount of research data available on this component, particularly in a composite arrangement.

The ABS sample was sourced from plastics distributor Vink [81] and was confirmed to contain the following distribution of base polymers;

- Styrene – 58-63%
- Acrylonitrile – 20-25%
- Butadiene – 16-21%
- Additives – 1-4%

The bubble wrap sample was sourced from Flexocare [82] and is formed of polythene. Cardboard used for testing was sourced from spare cardboard packaging found within the Lund University Laboratory. The cardboard was from the same source and of the same design, as shown in Figure 10, throughout the testing. A risk assessment of the materials tested was conducted prior to undertaking laboratory work as provided in Section 9.

Sample thicknesses did not impact the distance of the sample from the cone heater. This was due to the refractory blankets inserted under the samples to compensate for the different material thicknesses tested as per the guidance of ISO5660-1:2015.

The samples were conditioned in the Lund University conditioning chambers as shown in Figure 11. Conditioning was conducted as per Section 8.2 of ISO5660-1:2015 and ISO 554-1976 whereby conditions were set to temperatures of 23°C, relative humidity of 50% and a pressure of between 86 and 106 kPa. Test specimens were weighted, then left in the chamber for a minimum of 24 hours before being reweighed to ensure that there was not a change in weight greater than 0.1 gram or 0.1% of sample mass.

Figure 11 Conditioning chamber

All samples were of dimensions of 100mm by 100mm and were prepared in accordance with the guidance of ISO5660-1:2015. Prior to testing, the samples were prepared by wrapping in aluminium foil. ISO 5660-1:2015 notes that the results of testing will be of limited value should the sample melt over the rim of the sample holder. This was identified as a risk to the samples tested and therefore suitable sample preparation was imperative. The sample, after being wrapped in foil with the underside left exposed and installed into the sample holder retainer frame, was covered with layers of refractory fibre blanket until between one and two layers of the blanket were extended above the rim of the frame.

Section 3.4 - Experimental procedure

After samples were appropriately conditioned and prepared, the test procedure, as per the guidance of ISO5660-1:2015, was followed with procedural alterations as recommended by Werrel (70) for open CACC apparatus. To avoid unnecessary repetition the reader is directed to Section 2.2.2 for further discussion regarding the procedure adopted for the CC and CACC tests.

As per the ISO5660-1:2015 test procedure when flaming ignition was present for at least 10 seconds the spark igniter is removed and the sample is considered ignited. When flaming ceases for at least 10 seconds due to self-extinguishment the spark igniter is reintroduced for the remainder of the test. The test runs for at least 30 minutes and at least 120 seconds of data is collected after flameout.

To avoid drafts within the CC experiments the doors to the lab were not fully open with only enough of a gap left to allow gradual replacement air to enter the lab as the extract fan removed the products of combustion. Due to the distance between the door and the CC this is considered to have no effect on results.

In Section 9 a laboratory schedule has been provided to illustrate the extent of experimental work conducted over the allocated time period within the laboratory.

Section 3.5 - Calculation of Nitrogen flow rates

An altered oxygen mass fraction within the controlled atmosphere chamber was used to demonstrate changing material behaviour under typical hypoxic conditions. The oxygen concentrations compared are 20.95%, 17% and 15%. Tests were also conducted at different radiant heat fluxes of 25kW/m^2 and 50kW/m^2. The CACC collected output data on the oxygen consumption, CO yield and mass loss of the sample which were then used to analyse results.

The necessary balance of N_2 to air flow rates required to achieve the required oxygen concentration in the controlled atmosphere chamber were calculated as per the procedure given in the '*Users' guide for the low oxygen cone calorimeter attachment'* (FTT Ltd., (83)). The flow rates were calculated as;

$$\dot{V}_N + \dot{V}_A = \dot{V}_T \qquad \text{Equation 26}$$

$$C_{O_2} = \frac{0.2095 \cdot \dot{V}_A}{\dot{V}_A + \dot{V}_N} \cdot 100 \qquad \text{Equation 27}$$

$$\dot{V}_A = \frac{\dot{V}_T}{20.95} \cdot C_{O_2} = 8.592 \cdot C_{O_2} \qquad \text{Equation 28}$$

When $\dot{V}_A$ is calculated using Equation 28 then $\dot{V}_N$ can be calculated using Equation 26. The total flow rate, $\dot{V}_T$, has been set to 140 l/min. The reason for this choice is because it is the highest flow rate achievable with the N_2 rate supplied from the available cylinders at both 17% and 15% O_2. A higher flow rate is desirable to avoid stagnant zones within the chamber as described by Marquis (7). Using a flow rate of 140 l/min the equations above give the following values at 17% and 15%:

17% O_2 = $\dot{V}_A$= 113.6 l/min or 1.89 l/s

$\dot{V}_N$ = 26.39 l/min or 0.44 l/s

15% O_2 = $\dot{V}_A$= 100.23 l/min or 1.67 l/s

$\dot{V}_N$ = 39.76 l/min or 0.66 l/s

These theoretical values do not necessarily correspond to the exact values for the chamber due to localised leakage from the chamber. Therefore, the calculated value was revised to ensure that the chamber O_2 concentration was at the correct percentage ($\pm 0.2\%$). The flow rate was set on the flow rate control panel and was monitored on the oxygen analysers located before and after flow into the chamber as shown in Figure 12.

Figure 12 Entire CACC setup (N_2 cylinders and flow control on left of image and O_2 analyser on the right)

Once the sample was introduced into the chamber there was a period where it was exposed to preheating from the cone heater even when the radiation shield is used. This period is unavoidable as it is necessary to reintroduce equilibrium into the chambers atmosphere which was disrupted when the door to the chamber is opened to insert the sample. To minimise the time of preheating, whilst ensuring that equilibrium is reached, three trial runs were undertaken.

In the time trials, to determine the time necessary for equilibrium, the lowest O_2 level was used (representing the controlled atmosphere which would take the longest time to regain equilibrium) with the door left open for a worst case of 20 seconds. The three-time trials measured to see how long it took for equilibrium to be reached once the door was opened, the sample was inserted and then the door closed again. A worst case of approximately 40 seconds to reach equilibrium again was found from the three trials and therefore 45 seconds was used for each test. To make sure uniformity was observed in the tests the measured data would not begin until 45 seconds after the closure of the chamber door. Figure 13 demonstrates how these periods are registered in the HRR data collected by the CACC.

It is noted that the 45 second exposed to heated conditions, albeit with the protection of the CC shield, was not replicated in the ambient cone calorimeter samples. This was due to the logistics of the testing procedure necessitating that the CC tests were completed before the CACC tests and therefore the exposure time of 45 seconds had not yet been calculated. This adds some discrepancy between tests, however, it is still considered reasonable to compare results for the purpose of this study as the extra heating exposure does not impact the general behaviours observed.

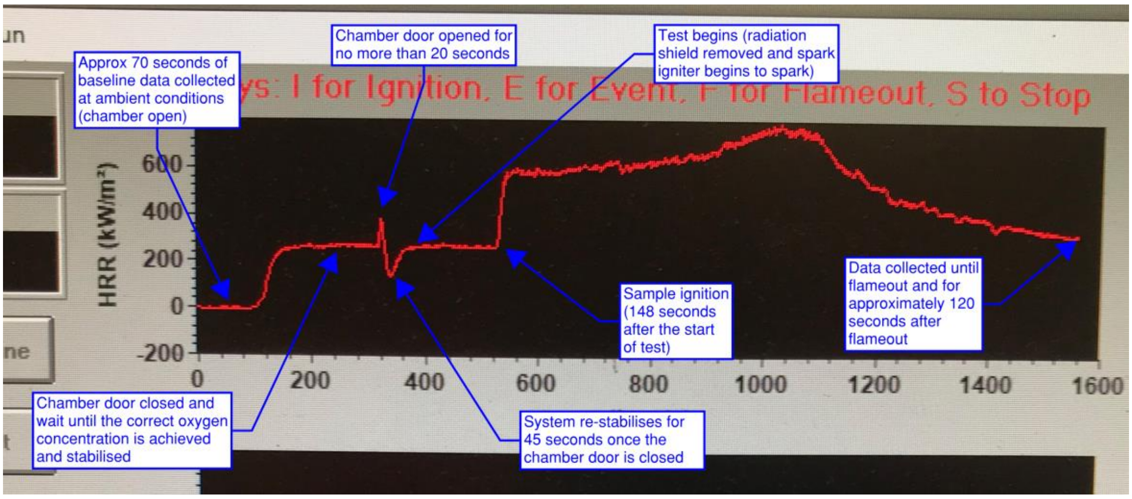


Figure 13 The equilibrium and baseline times as shown in raw HRR data

Section 3.6 - Mitigating experimental uncertainty

During the experimental procedure the samples burning behaviours were recorded on video for later review. Written notes were also taken of observations made during the test. The tests lasted for a maximum of approximately 15-45 minutes.

In order to limit experimental uncertainty three versions of the same sample were prepared and tested in the same conditions in order to identify numerical outliers in the data collected. The number of reruns of the same experiment were in accordance with the typical recommendations of ISO5660-1:2015 and the full three tests were conducted for 16 of the 18 test sets completed.

Due to time limitations imposed for laboratory work from the Covid19 pandemic some retests were not completed as a reduced laboratory schedule needed to be enforced. Figure 14 and Figure 15 show typical examples of the similarity of ABS and composite samples throughout the full range of tests conducted. It was noted that this produced consistent results for pure samples of ABS but did not fully capture the variability of the composite sample behaviour. It is therefore recommended that composite samples featuring multiple layers of sample materials are retested more than three times to ensure that the variability of material behaviour is fully captured. The effect of the composite sample material behaviour on burning variability is discussed further in Section 5 data analysis.

It is noted that experimental uncertainty could be further mitigated through the use of statistical analysis to quantify variables within the tested arrangement. It was decided that due to the limited scope and timescale of the study, the well-established nature of the equipment used and the lack of statistical analysis in similar studies released in the research community, that no statistical analysis would be conducted in this instance.

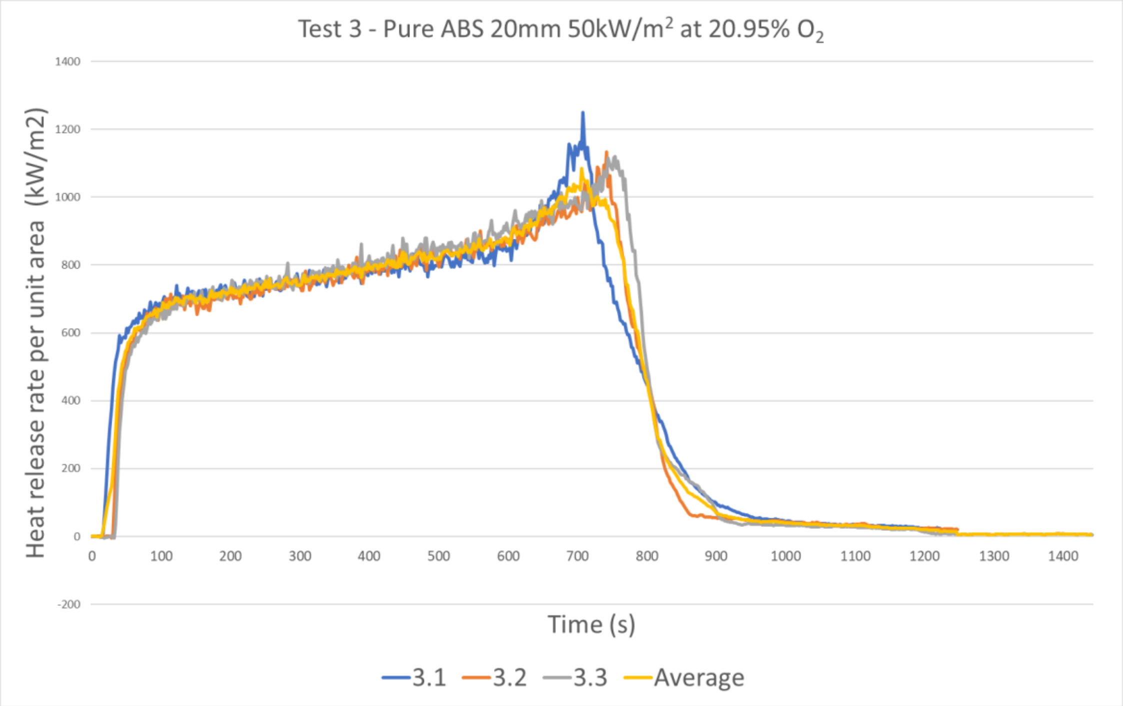


Figure 14 Similarity between test repeats on ABS samples

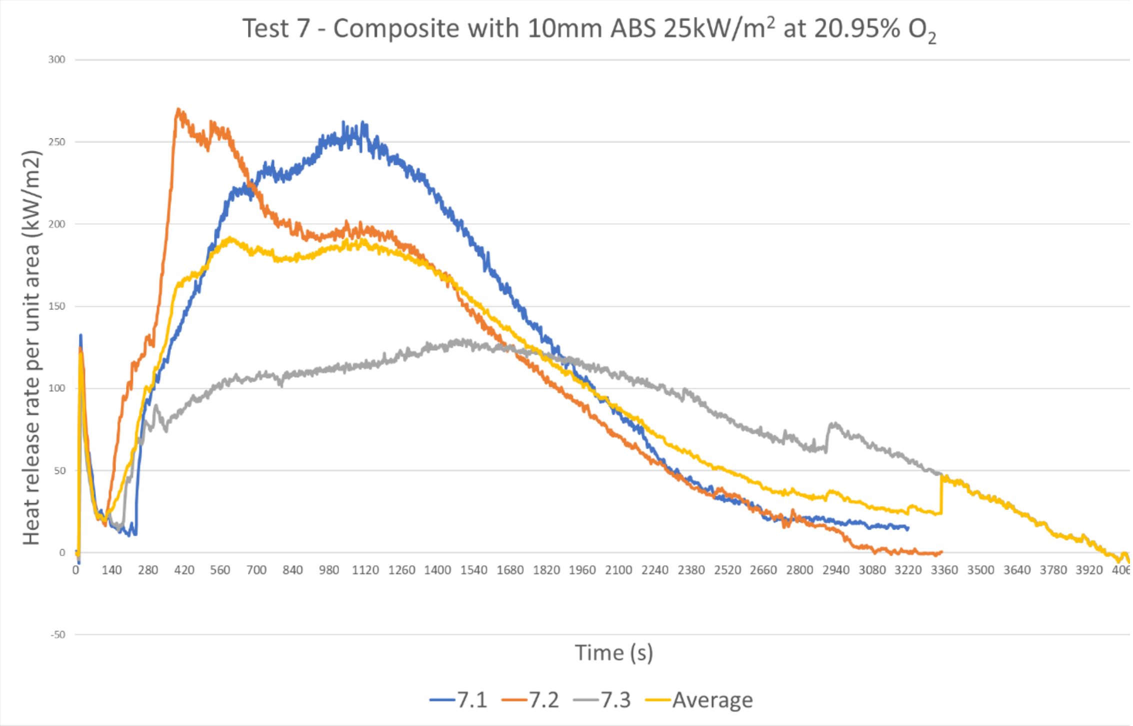
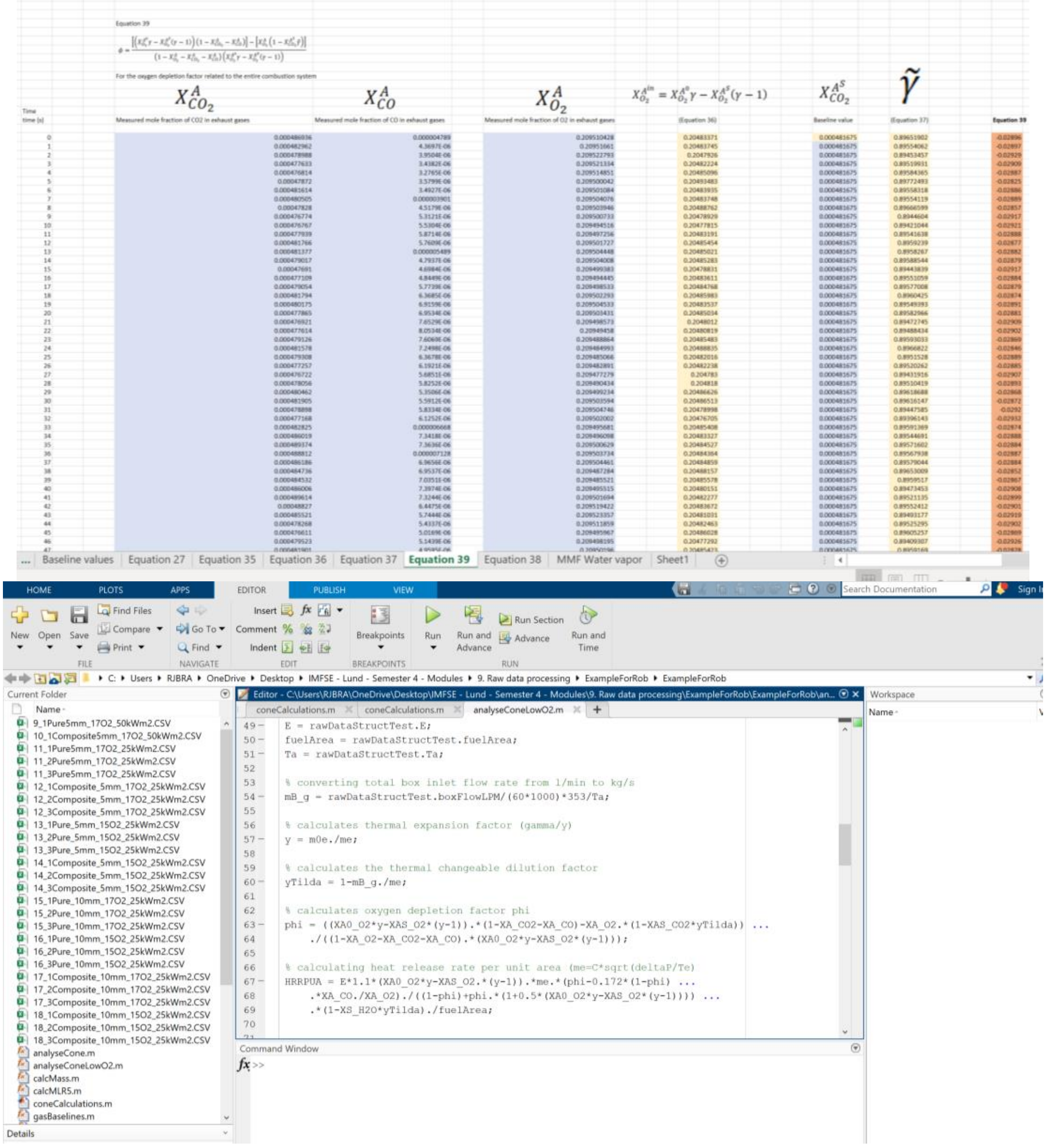


Figure 15 Similarity between test repeats on composite samples

Section 3.7 - Data processing procedure

Data processing was conducted using the program MATLAB, using a script developed by Madsen et al at Lund University (84). The calculations were coded into the software and then used for data processing after the experimental data had been collected. The calculations coded into the MatLab software were those initially proposed by Werrel(70) for the open CACC procedure. To ensure that potential errors in the calculation procedure were accounted for the equations were also independently calculated using an excel file developed during the thesis project. The results independently calculated using matlab and excel as shown in Figure 16, were compared with an example of the final HRR data shown in Figure 17. This process allowed calculation uncertainty to be reduced since the two scripts demonstrated sufficient similarity.



```
E = rawDataStructTest.E;
fuelArea = rawDataStructTest.fuelArea;
Ta = rawDataStructTest.Ta;

% converting total box inlet flow rate from l/min to kg/s
mB_g = rawDataStructTest.boxFlowLPM/(60*1000)*353/Ta;

% calculates thermal expansion factor (gamma/y)
y = m0e./me;

% calculates the thermal changeable dilution factor
yTilda = 1-mB_g./me;

% calculates oxygen depletion factor phi
phi = ((XA0_O2*y-XAS_O2*(y-1)).*(1-XA_CO2-XA_CO)-XA_O2.*(1-XAS_CO2*yTilda)) ...
    ./((1-XA_O2-XA_CO2-XA_CO).*(XA0_O2*y-XAS_O2*(y-1)));

% calculating heat release rate per unit area (me=C*sqrt(deltaP/Te)
HRRPUA = E*1.1*(XA0_O2*y-XAS_O2.*(y-1)).*me.*(phi-0.172*(1-phi) ...
    .*XA_CO./XA_O2)./((1-phi)+phi.*(1+0.5*(XA0_O2*y-XAS_O2*(y-1)))) ...
    .*(1-XS_H2O*yTilda)./fuelArea;
```

```
>>
```

Figure 16 Visual showing the two methods of data processing used excel (upper) and matlab (lower)

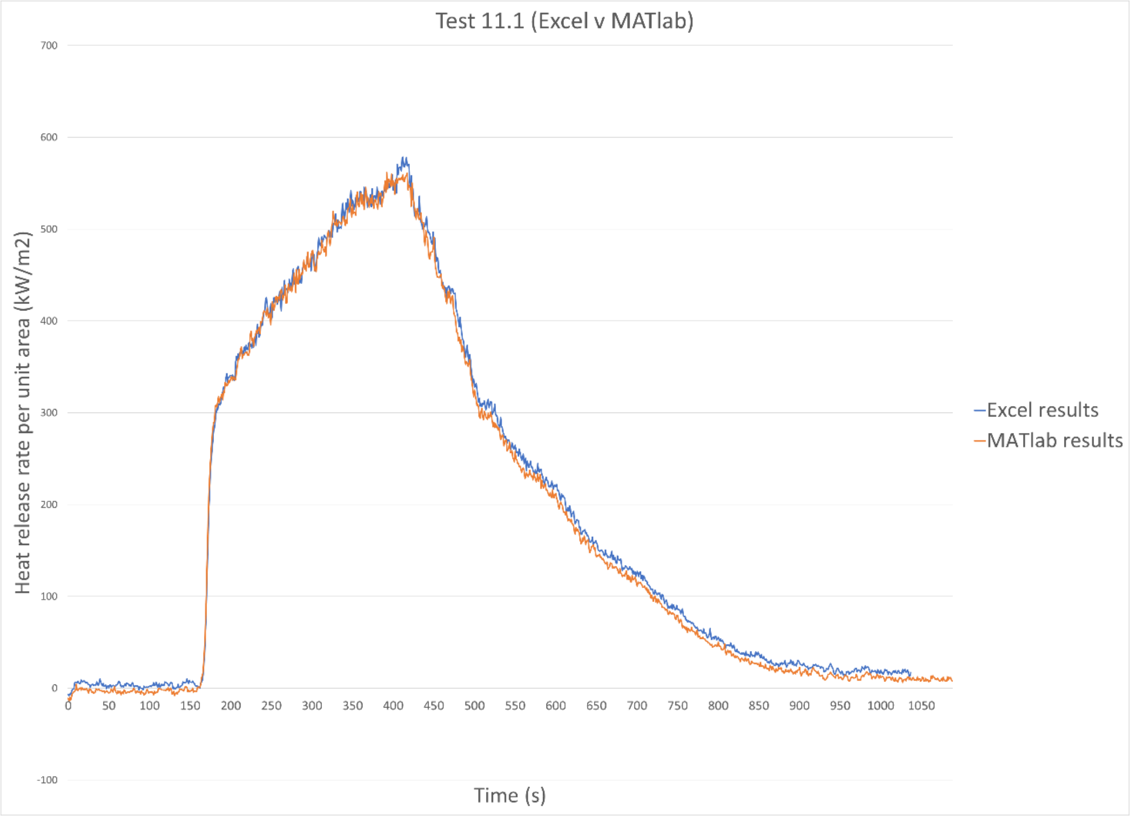


Figure 17 Comparison between excel and matlab results for Experiment 11.1

The two independently formulated scripts produced similar outputs with minor differences likely due to small discrepancies between the timesteps used for baseline data. As the scripts demonstrate sufficient replicability of output it is considered reasonable to conclude that the calculation procedure of Werrel (70) has been correctly followed and that no additional uncertainty was being introduced by through the calculation method.

Section 3.8 - Data smoothing

Data smoothing was applied to the mass loss rate data in order to reduce the noise of the readings taken from the load cell. A moving average was performed on the data with methods taken from ISO5660:2015 for applying a five-point numerical differential scheme on the mass loss rate data.

Section 4 - Experimental results

Section 4. 1 - Heat release rate experimental results at 20.95% O_2

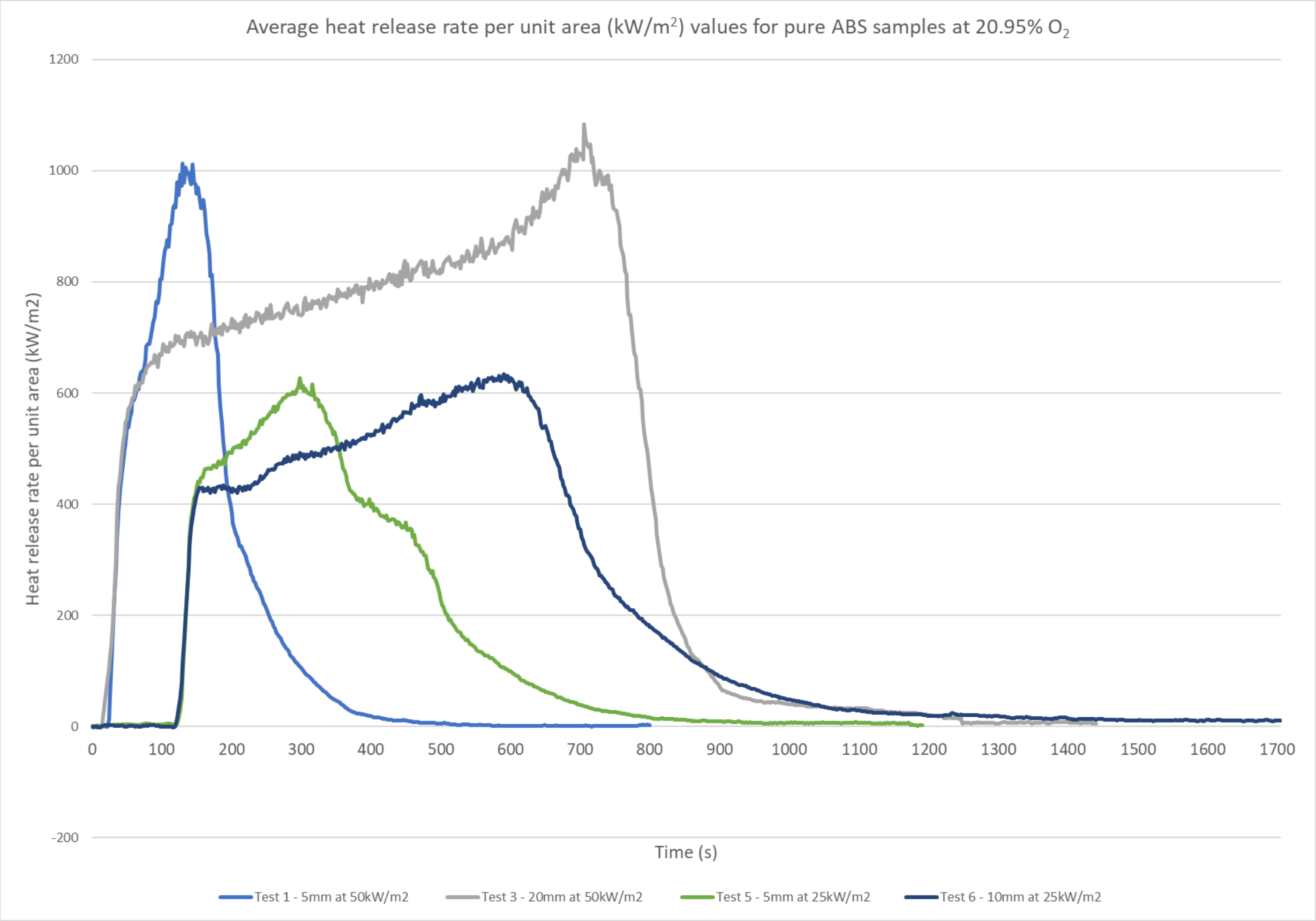


Figure 18 Average heat release rate per unit area results (averages between the three repeat tests) from pure samples at O_2 = 20.95%

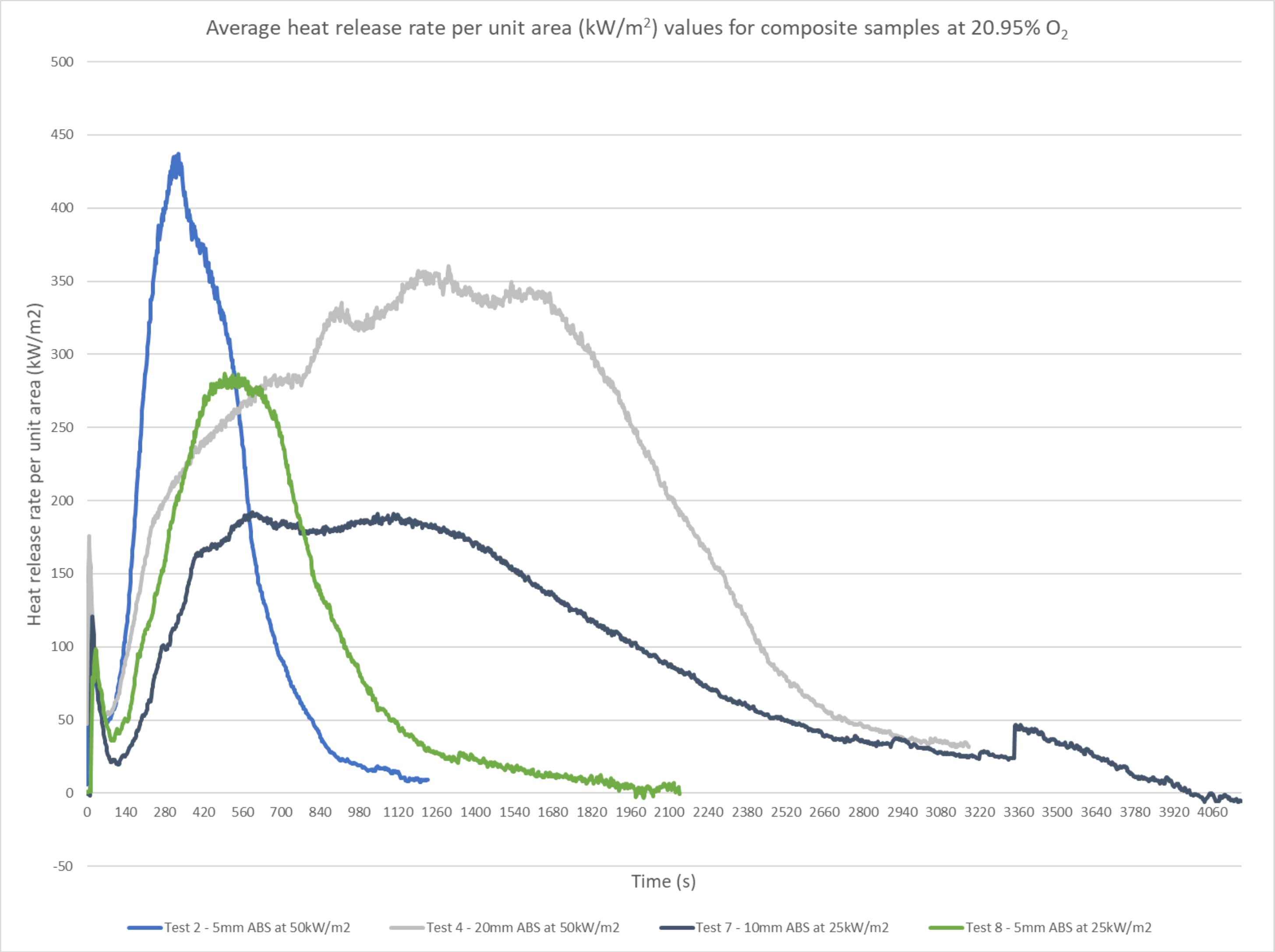


Figure 19 Average heat release rate per unit area results (averages between the three repeat tests) from composite samples at O_2 = 20.95%

Section 4.2 - Heat release rate experimental results at 17% O_2

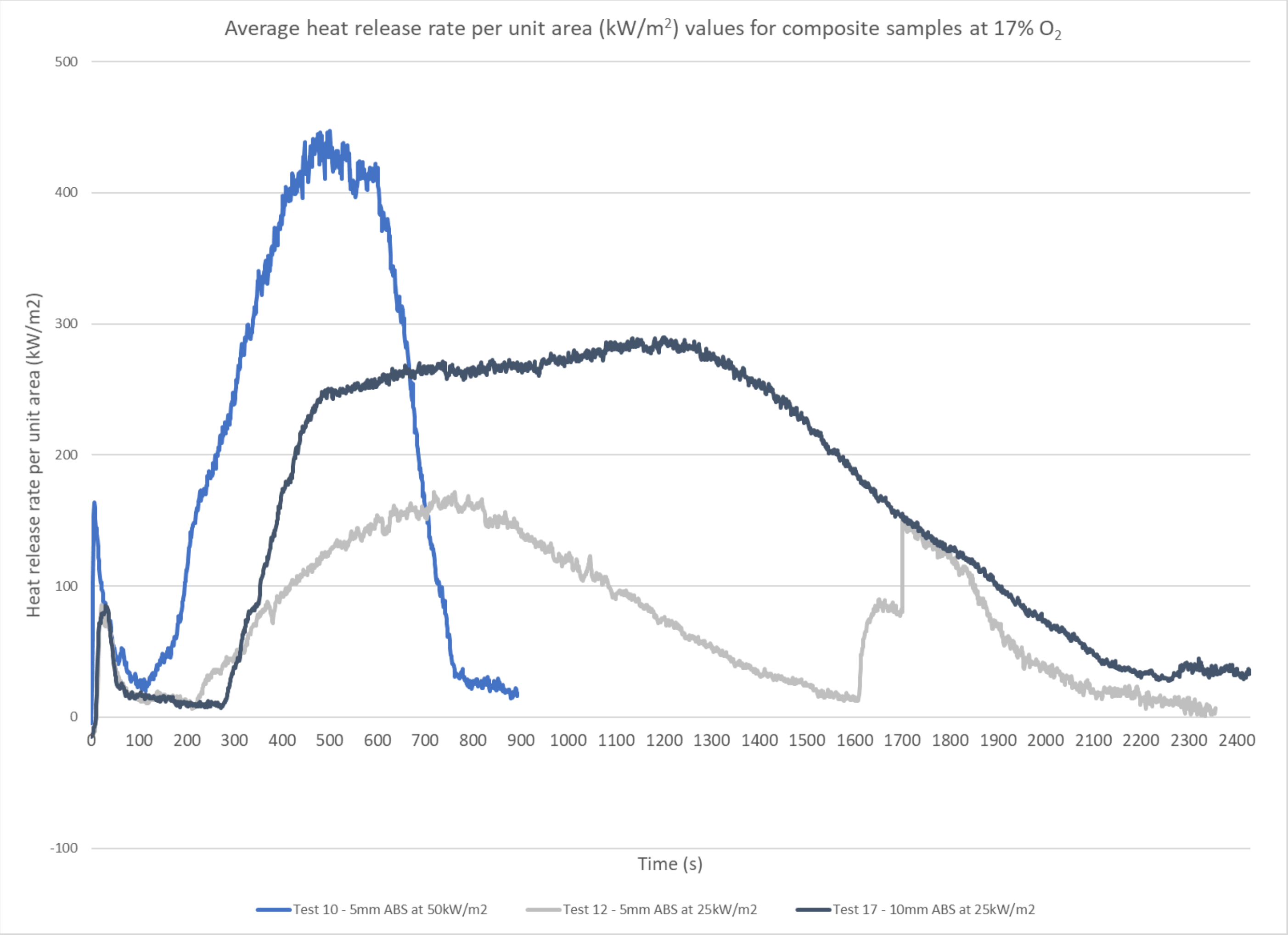


Figure 20 - Average heat release rate per unit area results (averages between the three repeat tests) from composite samples at O2 = 17%

Due to the limited page count for the following project further figures can be found in Section 9.5 with further data also available upon request.

Section 4.3 - Experimental results table

Primary test reference number	Secondary test reference number	Oxygen concentration	Material description	Heat cone irradiance	Sample weight	Ignition time	Flame out time	Max HRR measurement (kW/m^2)	Sample self-extinguishes?
1	1	20.95	ABS 5mm	50kW/m^2	49.9g	25	376	1089.24	No
	2				51.4g	23	553	1068.95	No
	3				46.1g	27	547	1022.26	No
2	1	20.95	Composite (5mm ABS)	50kW/m^2	63.2g	7	999	597.51	No
	2				53.8g	9	852	425.69	No
	3				62.8g	11	873	521.8	No
3	1	20.95	ABS 20mm	50kW/m^2	201.2g	20	1037	1248.8	No
	2				198.8g	30	1054	1134.04	No
	3				200.4g	33	942	1120.27	No
4	1	20.95	Composite (20mm ABS)	50kW/m^2	208.8g	6	2735	444.64	No
	2				207.3g	5	2917	367.59	No
	3				209.7g	6	2881	357.35	No
5	1	20.95	ABS 5mm	25kW/m^2	50.5g	132	962	729.65	No
	2				73.1g	125	932	716.21	No
	3				50.6g	132	799	668.88	No
6	1	20.95	ABS 10mm	25kW/m^2	101.3g	122	1347	645.8	No
	2				105.1g	129	1408	712.8	No
	3				99.3g	132	1064	667.71	No
7	1	20.95	Composite (10mm ABS)	25kW/m^2	116.9g	15 & 232	200 & 2649	262.2	Yes, 200
	2				116g	13 & 122	110 & 3087	270.25	Yes, 110
	3				107.1g	17 & 192	85 & 3968	129.96	Yes, 85
8	1	20.95	Composite (5mm ABS)	25kW/m^2	60.7g	28	1128	352.7	No
	2				66.8g	23	1659	335.1	No
	3				61.5g	19 & 155	114 & 1910	234.78	Yes, 114s
9	1	17.0%	ABS 5mm	50kW/m^2	56g	31	614	833.7	No
	2								

	3								
10	1	17.0%	Composite (5mm ABS)	50kW/m^2	66g	5	893	447.12	
	2								
	3								
11	1	17.0%	ABS 5mm	25kW/m^2	65.7g	170	1088	561.75	No
	2				60.6g	140	1066	543.72	No
	3				64g	184	1028	557.87	No
12	1	17.0%	Composite (5mm ABS)	25kW/m^2	57.6g	23 & 1661	90 & 2356	156.35	Yes, 90s
	2				65.2g	22 & 336	57 & 1699	254.37	Yes, 57s
	3				62.7g	21 & 239	64 & 1513	272	Yes, 64s
13	1	15.0%	ABS 5mm	25kW/m^2	56.2g	142	1107	554.97	No
	2				50.5g	150	1145	515.64	No
	3				60.6g	151	1078	594.44	No
14	1	15.0%	Composite (5mm ABS)	25kW/m^2	57.5g	20 & 926	61 & 1653	204.4	Yes, at 61s
	2				68.7g	10 & 824	55 & 3150	259.38	Yes, at 55s
	3				75.9g	15	43 (never reignites)	92.38	Yes, at 43s
15	1	17.0%	ABS 10mm	25kW/m^2	109.2g	163	1522	524.84	No
	2				108g	148	1608	529.76	No
	3				109.7g	136	1633	501.82	No
16	1	15.0%	ABS 10mm	25kW/m^2	110.1g	147	1493	441.16	No
	2				107.4g	157	1891	436.16	No
	3				109.3g	161	1802	443.58	No
17	1	17.0%	Composite (10mm ABS)	25kW/m^2	125.8g	24 & 369	54 & 2429	314.3	Yes, 54s
	2				120g	21 & 302	73 & 2281	316.85	Yes. 73s
	3				123.3g	13 & 314	55 & 2267	308.31	Yes, 55s
18	1	15.0%	Composite (10mm ABS)	25kW/m^2	122.4g	NA	NA	NA	NA (never ignites)
	2				123.7g	16 & 339	44 & 2494	327.44	Yes, 44s
	3				123.3g	17 & 649	44 & 2417	325.24	Yes, 44s

Table 2 Experiment results summary

Section 5 - Results analysis

Section 5.1 - Importance of material thickness

One of the variables altered during testing was the thickness of the ABS in both tests consisting of pure ABS and composite materials, featuring a top layer of cardboard and bubble wrap. ABS thicknesses ranged from 5mm to 20mm. The effect of material thickness is immediately evident for pure ABS samples in ambient conditions (Tests 1 and 3 found in Section 9.5) with the 5mm sample rapidly achieving its peak HRRPUA value before immediately displaying rapid HRRPUA reduction. This short, sharp rise and fall in HRRPUA is in contrast to the thermally thick 20mm sample which displays an extended period of relative equilibrium. The 20mm sample is thermally thick and displays semi-infinite behaviour with the peak HRRPUA occurring at the end of the burning period where the fuel source has been reduced in thermal thickness such that it performs like its thermally thin counterpart and burns away the remaining fuel source.

Similar behaviour is observed in composite samples with the thermally thin test samples reaching flameout much faster and maintaining peak HRRPUA values for less time. However, the ignitability of composite samples and the variability with regard to thermal thickness, displayed a wider range of results between tests in ambient and hypoxic conditions, than observed for pure ABS samples.

Thermal thickness and ignition/flameout time

From reviewing Table 1 it is clear that thermal thickness effects the flameout time but the changes to the ignition times are negligible in pure ABS samples. This is true in all variable cases and suggests that, while the material thickness is varied between tests this is only one component of thermal thickness. The total thermal thickness is not varied to such an extent that heat losses from the material surface are significant enough to prevent or delay igniting the material surface. However, the flameout times are significantly enhanced where the material is thermally thicker as there is more burning material available to sufficiently sustain burning via the production of volatiles to the flaming region.

Interestingly, the tests conducted suggest that composite samples of 10mm ABS were more likely than composite samples with 5mm ABS to self-extinguish in ambient conditions (both thicknesses performed similarly in this regard in hypoxic conditions with all samples self-extinguishing after the initial burning period of the top layer of cardboard). This suggests that in a composite arrangement, with an ash forming layer, the increased heat lost from absorption to a thermally thicker underlying layer could prevent sustained combustion. Where there is a thermally thinner layer underneath there is less heat absorption into the ABS and therefore more chance to sustain the heat necessary for pyrolisation at the surface leading to ongoing flaming. Evidently thermal thickness has had more of an effect on the reignition times of composite samples (regarding the secondary ignition of the ABS layer) than pure samples in the tests conducted.

Equation 10 notes the importance of density in thermal thickness. This can be observed in Test 5 as visualised in Figure 21 where one sample of the same size and thickness but a greater mass (approximately 70g rather than 50g) shows a notably increased burning time over the test. This is a good example of the reliance of material burning behaviour on thermal thickness as the performance of Test 5.2 is much different than other repeat tests. This is particularly stark due to the typical uniformity observed between repeat tests of pure ABS throughout the rest of the testing regime.

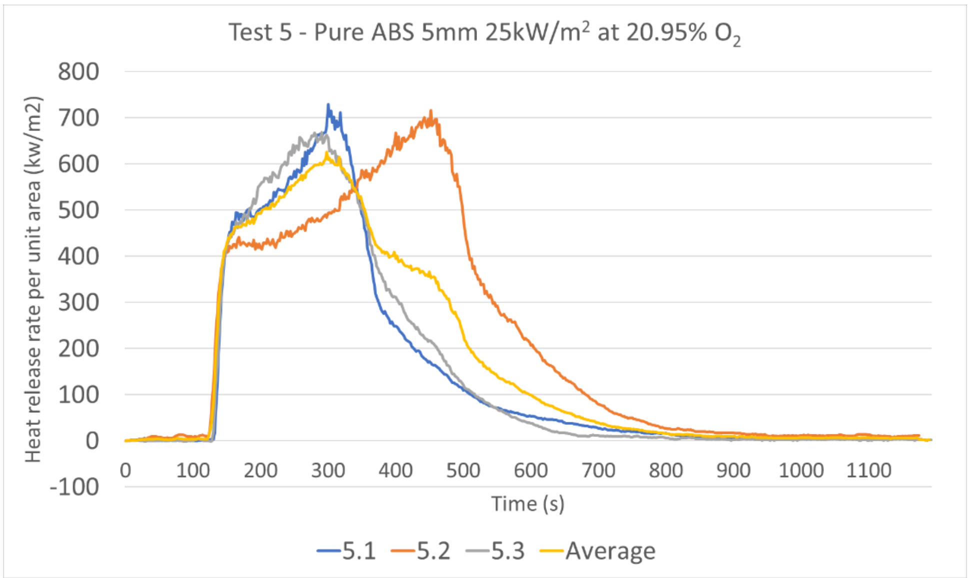


Figure 21 The impact of sample thermal thickness on test set 5

Influence of thermal thickness on the peak HRRPUA values over the tests

The results indicate that the thermal thickness of materials has a different relationship between burning samples in ambient conditions than in hypoxic conditions. This is also influenced on whether the material contains composite layers or a single layer of pure material.

Thermally thick and thin samples of pure ABS demonstrate the same peak HRRPUA values in ambient conditions but not in hypoxic conditions where thermally thin samples are shown to have higher HRRPUA values in pure samples. This is observed in oxygen concentrations of both 17% and 15% and is shown to increase in effect at lower O_2 concentrations. This is illustrated in comparisons of pure ABS at various oxygen concentrations in Figure 22.

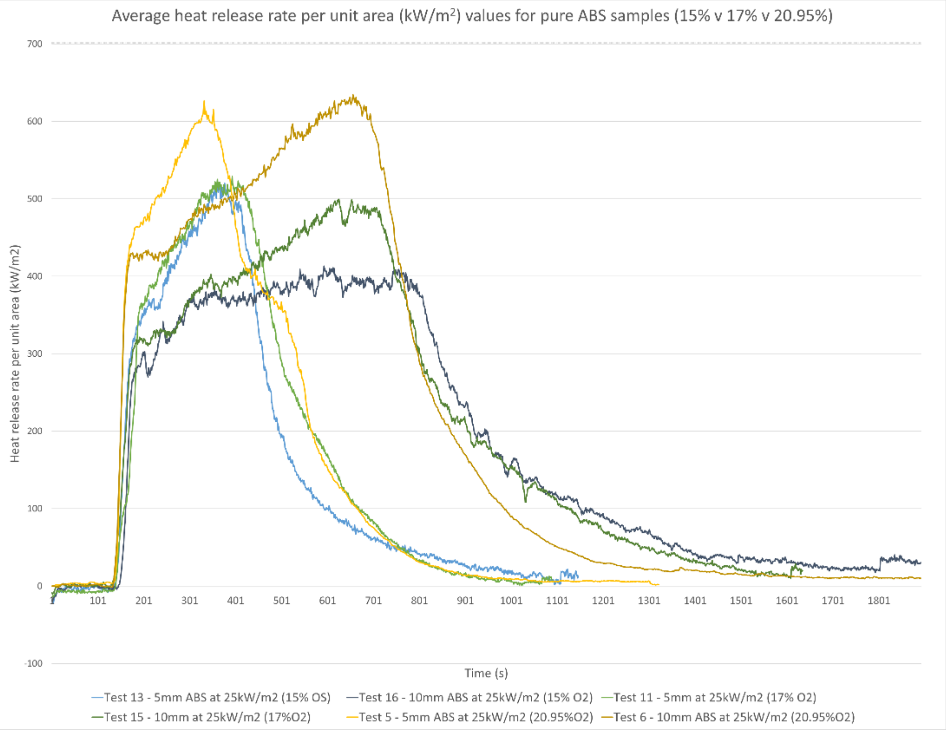


Figure 22 Comparison of thermal thicknesses at different oxygen concentrations for ABS samples

Thermally thicker samples clearly demonstrate a greater susceptibility to oxygen concentration with a more pronounced, steady decline in heat release rates as the oxygen concentration is reduced. This is as predicted within the theoretical discussions given in Section 2 as a reduction in the oxygen mass fraction lowers the B number of the fuel and subsequently reduces the heat release rate. As the HRR lowers the thermal thickness of the sample has a greater significance on the overall transference of heat internally within the sample. A greater total thermal inertia across the sample lowers the temperature of the exposed surface, as heat is absorbed into the samples, and further reduces the peak HRRPUA. At ambient conditions the equal HRRPUA peaks for different material thicknesses suggests that the thermal inertia of these samples are negligible compared to the burning rate of the fuel and that the thermal inertia becomes more critical to material burning behaviour as the oxygen mass fraction is lowered (lowering the HRRPUA).

Thermally thicker, pure samples were shown to increase the chance of self-extinguishment and lower the maximum HRRPUA under hypoxic conditions when no such effects were observed in thinner samples. The interrelationship of thermal thickness and oxygen percentage is integral to determining the effectiveness of an ORS through material testing due to the importance of material dimensions to the ignition threshold.

The relationship between the tested thicknesses of pure ABS samples was broadly similar with the thinner samples taking approximately half the time to begin the HRRPUA decline than that of the larger samples. This suggests that there is some difference in relative burning rates between ambient and hypoxic conditions (because the ambient samples compared were 5mm and 20mm rather than 5mm and 10mm) but the behaviour is broadly similar compared to the significant changes in burning relationship observed in composite samples where the O_2 concentration was altered.

The behaviour observed is different for composite samples as illustrated in Figure 23. For hypoxic conditions (both 17% and 15% O_2) the 5mm ABS composite samples burn at a lower HRRPUA than their respective 10mm version. This is in conflict with the behaviour observed for the pure samples. In ambient conditions, composite tests involving thermally thin samples have a lower HRRPUA during the initial 100 seconds of the test, where the cardboard top layer is observed to burn, but a higher HRRPUA for the ABS portion of burning behaviour. What also seems unusual at first inspection is that the peak HRRPUA for lower oxygen concentrations of thermally thick samples is higher than for the ambient samples. This is in stark contradiction to other tests throughout the study.

To summarise, the composite material tests were shown to contradict the pure sample tests in two ways;

1. Typical indications of thermally thick/thin behaviour, based on the thickness of the sample, are no longer clearly observed
2. Typical indications of effect of hypoxic conditions on HRRPUA are no longer clearly observed,

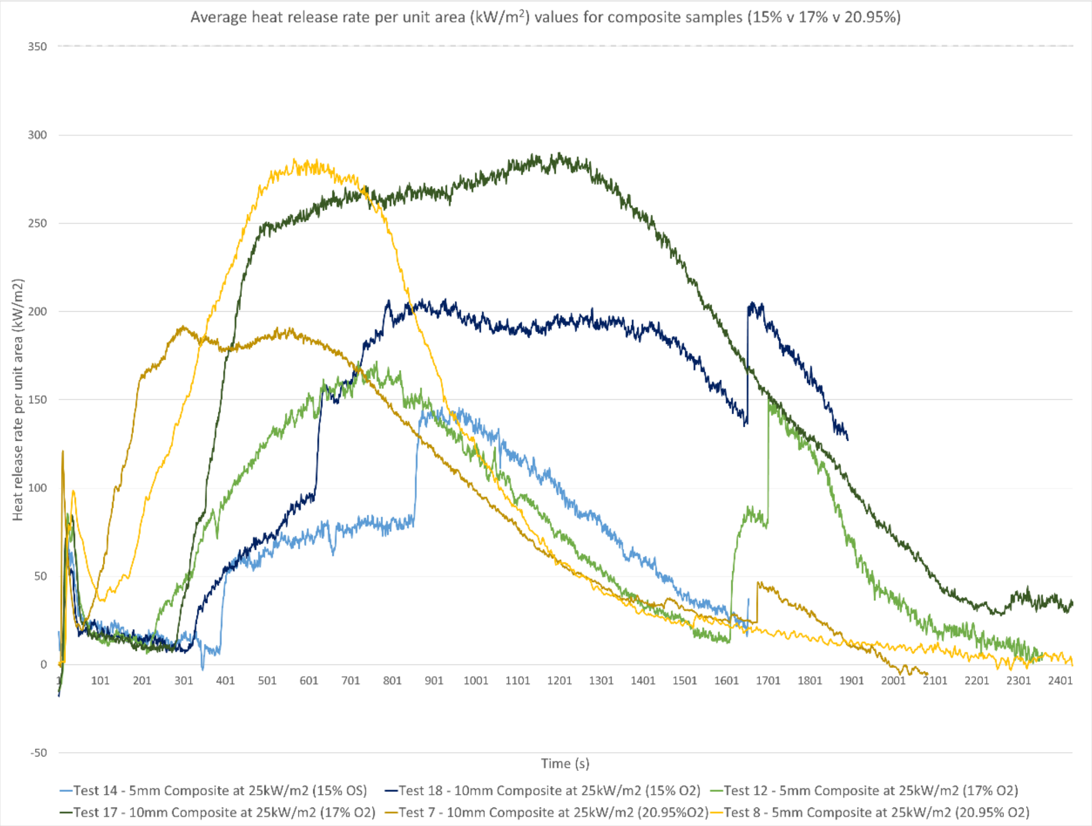


Figure 23 Comparison of thermal thicknesses at different oxygen concentrations for composite samples

It is theorised that there are two primary causes for the alteration of typical behaviour in composite samples exposed to hypoxic conditions. These are;

1. The initial burning of the cardboard layer, its combustion efficiency during this stage and the coverage of the subsequent ash layer created once the cardboard layer has been pyrolized.
2. The time between self-extinguishment of the initial flaming cardboard, caused by the development of the protective ash layer, and the reignition of the ABS due to the reintroduction of the spark igniter

Ambient conditions indicate better burning efficiency than hypoxic conditions. This is not only noted in the literature reviewed but is also indicated by the CO yield and levels of CO and CO_2 produced during the different tests conducted (see Figure 30 and Figure 31 respectively). The hypoxic test samples have a lower burning efficiency, which early into testing produces a thicker ash layer over the sample, causing samples of all thicknesses to self-extinguish early on in the test as the ash layer prevents the ABS below from being exposed to sufficient heat.

In the ambient oxygen percentage tests, less ash is created from the cardboard layer as the burning is closer to stoichiometry and it takes longer for the ash layer to inhibit the heating of the ABS layer below. Two out of three tests in ambient conditions of 5mm ABS saw the ABS heat sufficiently before the ash layer prevented sustained flaming. It is for this reason that composite samples with 5mm ABS behave similarly than observed in other tests as the burning of the ABS layer occurs prior to the development of the blanketing effect from the ash layer. The composite samples of 10mm ABS in ambient conditions take longer to heat due to a higher thermal inertia and therefore the blanket layer forms prior to sufficient heating from the flaming cardboard which causes self-extinguishment. However, due to a sufficient supply of oxygen in the local atmosphere reignition occurs almost immediately (with the time between self-extinguishment and reignition from 10-100 seconds). The sample therefore burns but at a slower rate due to the protective ash layer that has formed during the self-extinguishment process.

The reason why the reduced atmosphere tests observed HRRPUAs greater than the ambient tests for the thicker samples was due to the time delay between self-extinguishment and reignition (approximately 250-300s and 300-600s for 17% and 15% respectively). This extended time exposed to the cone heater allowed the samples to reach thermal equilibrium and therefore the full ABS content was fully heated by the time the sample reignited. The burning behaviours of the composite samples essentially disrupted to the typically expected consequences of material thermal thickness in two ways;

1. The formation of a top layer of ash over the ABS prevented thermally thin samples from rapidly heating such that a short peak of HRRPUA area was observed as expected from thermally thin samples.
2. The heating of the sample between self-extinguishment and reignition, caused by the hypoxic conditions, prevented thermally thicker composite samples from demonstrating typical behaviour as thermal equilibrium was reached throughout the sample over the time leading up to reignition.

The result of the deviation from typical burning behaviour caused by a combination of composite layers and hypoxic conditions is the following;

1. Material behaviour of composite materials cannot be assumed to be the same between ambient conditions and hypoxic conditions due to the variation of exposure effects acting on the materials.
2. In some cases, hypoxic conditions may cause higher heat release rates than for the same arrangement in ambient conditions. Whilst this seems contrary to theoretical basis of ORS, and typical findings for pure materials in hypoxic conditions, the exposure to preheating overcoming material temperature gradients due to delayed reignition from a hypoxic environment could produce greater heat outputs in some cases.

Evidently bench scale testing does not necessarily translate to real world material performance. However, the indications made through the experimental tests on horizontal composites show material behaviours which could also be expected to be repeated on larger samples (namely, the build-up of a protective layer of post-combustion deposits). Therefore, the orientation and composite arrangement, and the material performance subsequently observed, provides useful findings that relate to larger scale problems which could be found in ORS design.

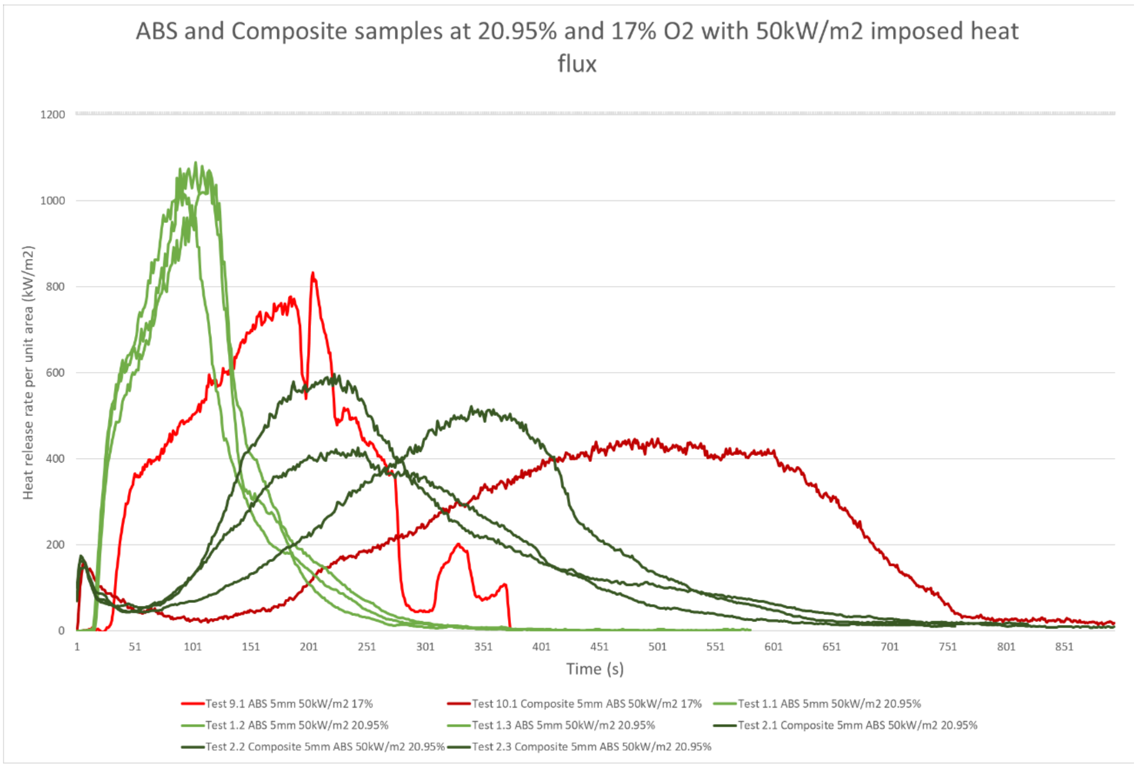
Section 5.2 - Impact of irradiance

Two irradiance levels were used during the experimental schedule, with the cone heater set to either 25kW/m^2 or 50kW/m^2. As discussed in the experimental research reviewed in Section 2, increasing the applied radiant heat flux serves to increase the burning rate, heat release rate, mass loss rate, yields of CO, CO_2 and smoke produced.

Due to a reduced laboratory schedule, caused by the Covid19 pandemic, the extent of 50kW/m^2 experimental data was limited for oxygen concentrations below 20.95%. For the tests that were run at 17% O_2 with an irradiance of 50kW/m^2 no repeat tests were completed, which risks added uncertainty, and the test for the pure ABS 5mm sample needed to be ended early due to the amount of smoke produced deepening down past the hood of the CACC. Despite this, the data has been included for qualitative comparison with the caveat of uncertainty noted. Figure 24, which includes the aforementioned data, does suggest that the performance of the 50kW/m^2 heat flux, imposed in hypoxic conditions, performs similarly than observed in ambient conditions. Notably, the degree of magnitude to which the hypoxic conditions effect the total HRRPUA of each test is very similar between the two imposed heat fluxes used. All tests observed a 20-30% reduction in peak HRRPUA between the 20.95%O_2 and 17%O_2 equivalent samples (for example, Tests 1 and 9 in Figure 24) where the imposed heat flux remains the same.

The impact of irradiance on HRR and MLR values

Where the irradiance level is higher the HRRPUA is higher in all cases. A higher irradiance causes a steeper incline and decline of HRR/MLR/production rates and generally causes flameout to occur sooner as the fuel source is spent quicker. However, the results show that samples are more likely to self-extinguish, or have a prolonged delay in reignition, when a lower irradiance is applied to the burning sample. None of the composite samples in ambient oxygen concentrations self-extinguished when a heat flux of 50kW/m^2 was applied whilst 4/6 samples self-extinguished when the heat flux was 25kW/m^2. It is also noted that in some cases the heat flux supported ignition in certain oxygen concentrations and not others with failure to reignite being more common at 15% O_2 under irradiance of 25kW/m^2 than at 17% at the same level of irradiance. The experimental results generally support the findings of Xin and Khan(9) who noted that the oxygen concentration necessary to extinguish fires was a function of external heat flux imposed on the sample. Where a higher radiative heat flux was imposed the samples were shown to be less likely to self-extinguish due to the local oxygen concentration.



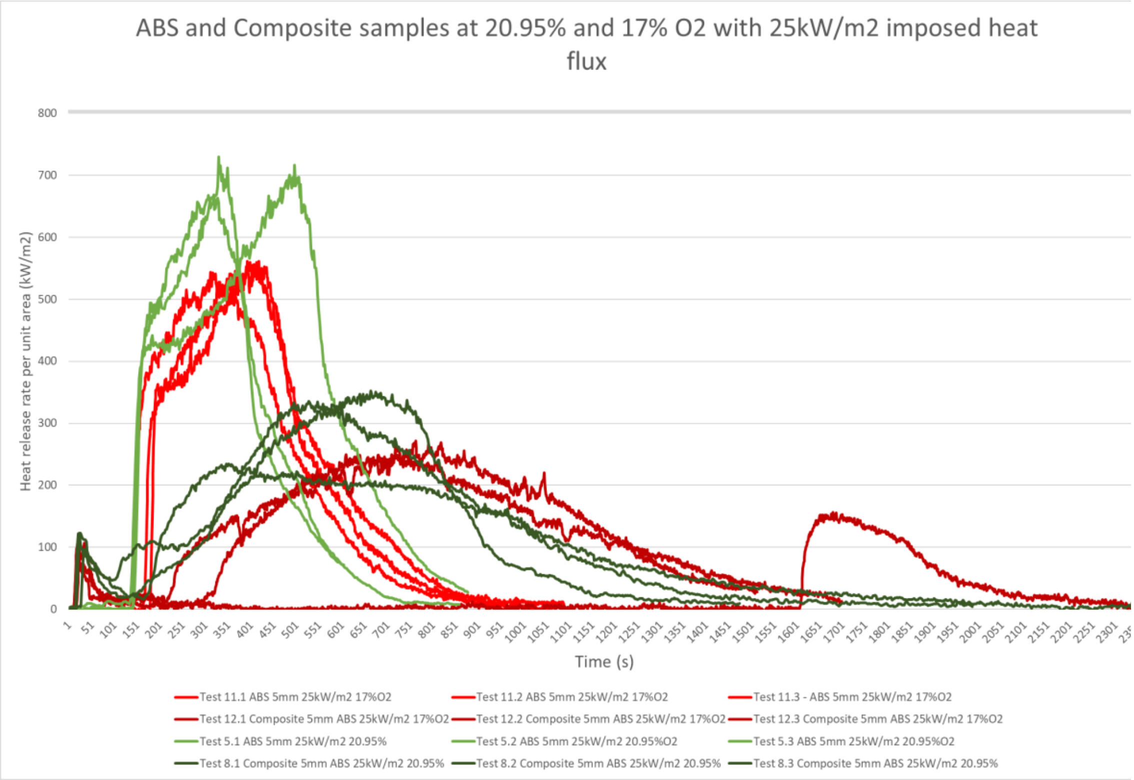


Figure 24 Comparison of the effect of variable heat flux on various tested samples

Figure 25 demonstrates that in some cases, where the samples did not ignite, mass loss still occurs within the sample even where there is no heat released (Test 18.1). This is as expected due to the decomposition of the sample as it is exposed to the irradiance of the cone heater. This effect, where the MLR and HRR do not mirror in general trend, only occurs in samples where there is an extended period of non-ignition and exposure to the cone heater. The reduction of oxygen concentration was sometimes shown prevent ignition due to the reduction in flame reaction rates as described by the Damköhler number described in Section 2.1.4.

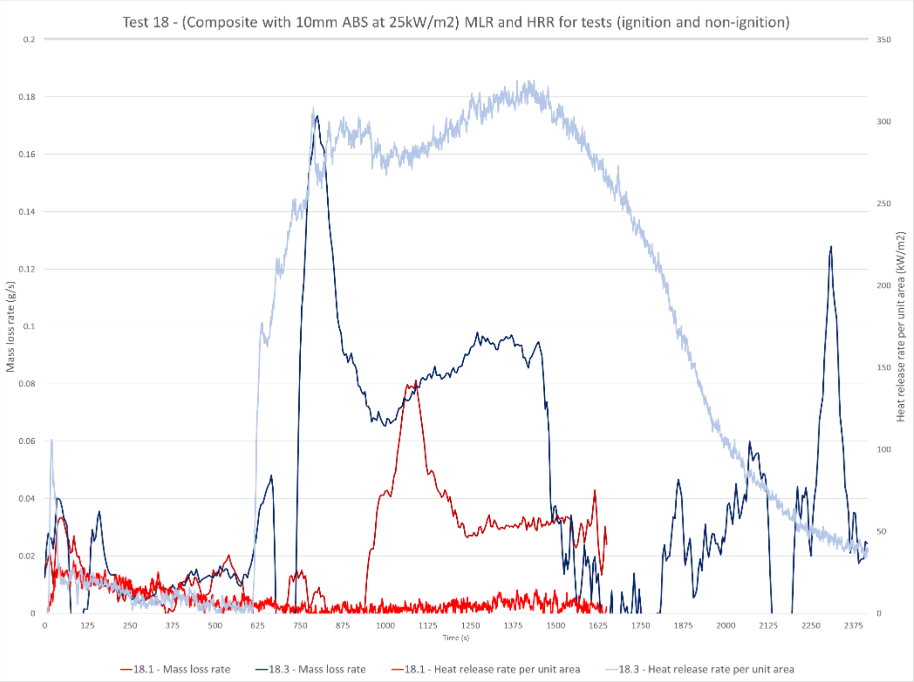


Figure 25 Comparison of HRR and MLR values in Test 18

The effect of irradiance on sample ignition times

It has long been known that the time to piloted ignition is a function of imposed heat flux and that once a critical heat flux is reached then piloted ignition can occur (Babrauskas and Parker(85)). This is observed in the experimental results with the time to ignition remaining unchanged between changes in irradiance levels in some instances. This behaviour is likely due to the surface layer material having a low enough thermal inertia to reach its critical heat flux instantaneously (i.e. cardboard) irrespective of the imposed heat flux applied. In other cases, where the surface layer material has a high enough thermal inertia that the critical heat flux is not immediately reached by the imposed heat flux levels, a range of ignition times are recorded which are dependent on the value of the imposed radiant heat flux and the time for the critical heat flux to be reached on the materials surface.

Effect of imposed irradiance on the production rates of species

The production of additional products of the combustion process, such as CO and smoke, occur due to the process of incomplete combustion. Where there is a lack of oxygen within the reaction process there is a formation of such species. In normal ambient conditions stoichiometry is not achieved due to temperature and concentration gradients in the burning region creating areas which are locally fuel rich, and thus, incomplete combustion occurs. In hypoxic conditions this occurs more readily due to the vitiated oxygen conditions. There is a lower mass fraction of oxygen and therefore larger regions where insufficient oxygen is present. However, irradiance causes the combustion process to occur with more thermal energy, and therefore, the vaporisation of more fuel. As smoke and CO are by-products of the combustion reaction where irradiance causes an enhanced rate of heat release the production of by-products also increases. As is demonstrated by Figure 27 whilst hypoxic conditions create a higher production of by-products associated with incomplete combustion it is the imposed irradiance which has a larger impact on the total production rate of these species.

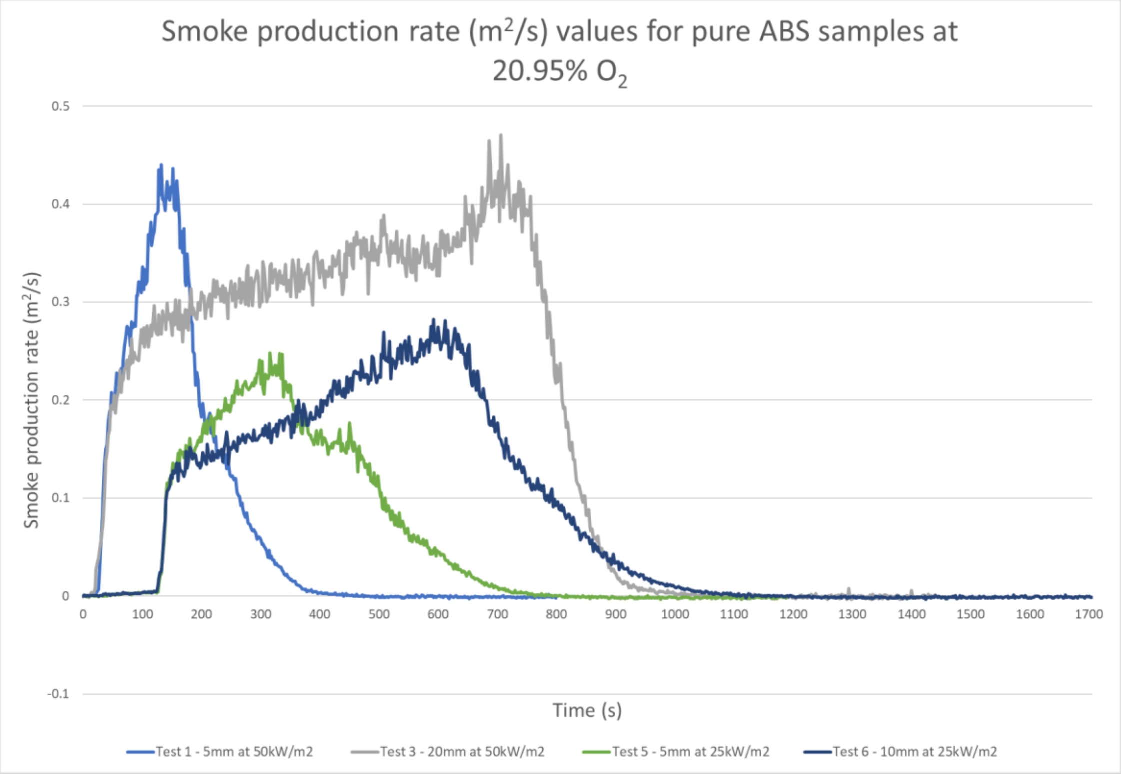


Figure 26 Smoke production rates for multiple samples at 25kW/m^2 and 50kW/m^2

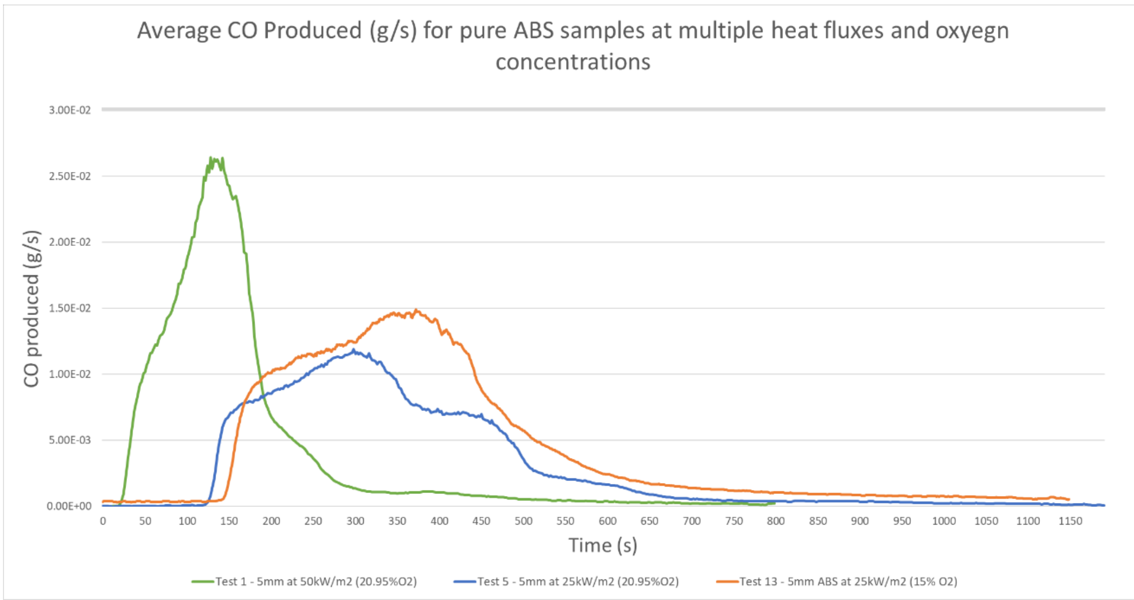


Figure 27 CO production rates for multiple samples at 25kW/m^2 and 50kW/m^2

Section 5.3 - Impact of composite layers

The impact of composite layers was determined to be one of the most significant factors which influenced the material burning behaviour of samples during the tests conducted. The composite layer altered the time to ignition with composite samples observing an earlier piloted ignition due to the negligible thermal inertia of the cardboard surface layer, where compared to the ABS layer, allowing a critical heat flux at the samples surface to be reached sooner. Once the cardboard and bubble wrap layers were fully pyrolyzed, which was a quick process due to the layers being thermally thin, the ash by-product of this process formed a protective layer over the ABS layer and caused the sample to self-extinguish. This was true for all samples in hypoxic conditions. Some of the composite samples in ambient conditions did not self-extinguish; particularly if a higher heat flux was used (0/6 self-extinguished) and if a 5mm ABS layer was used (1/3 of Test 8 self-extinguish). This is an important point to note as it demonstrates that if the tested composite sample is thinner than installed within the ORS (or the irradiance is unduly high) it may risk giving an incorrect indication of composite material performance and burning behaviour.

In some cases, for 15% O_2 hypoxic conditions, the composite sample did not ignite at all. This is another important point of note as all of the pure ABS samples ignited despite having a greater thermal inertia. In this instance it is thought that the cardboard surface layer decomposed due to exposure from the imposed heat flux from the cone heater prior to ignition from the spark ignitor (delayed due to the hypoxic conditions) and subsequently caused a protective layer of post decomposition by-product that blocked vaporisation of the ABS layer below. This is another indication that composite layers can lead to significant changes in material performance between ambient and hypoxic atmosphere performance.

The general burning behaviour was significantly different between the burning of pure samples and composite samples. Pure ABS samples burned with more intensity (during its peak almost observing laminar flaming) and less production of smoke. The flaming of the composite samples was more turbulent, less efficient and produced a greater volume of smoke. Figure 28 and Figure 29 indicate the behaviour in both cases. In composite samples there were instances where forces acting due to the reaction process, for example the pressure gradients and velocity of induced air, caused the displacement of the remaining by-products of combustion, as layers of ashen sample floated off of the sample holder. The expansion of the bubble wrap underlayer and cardboard layer caused the generation of bulbous peaks in the sample holder as shown in Figure 29.

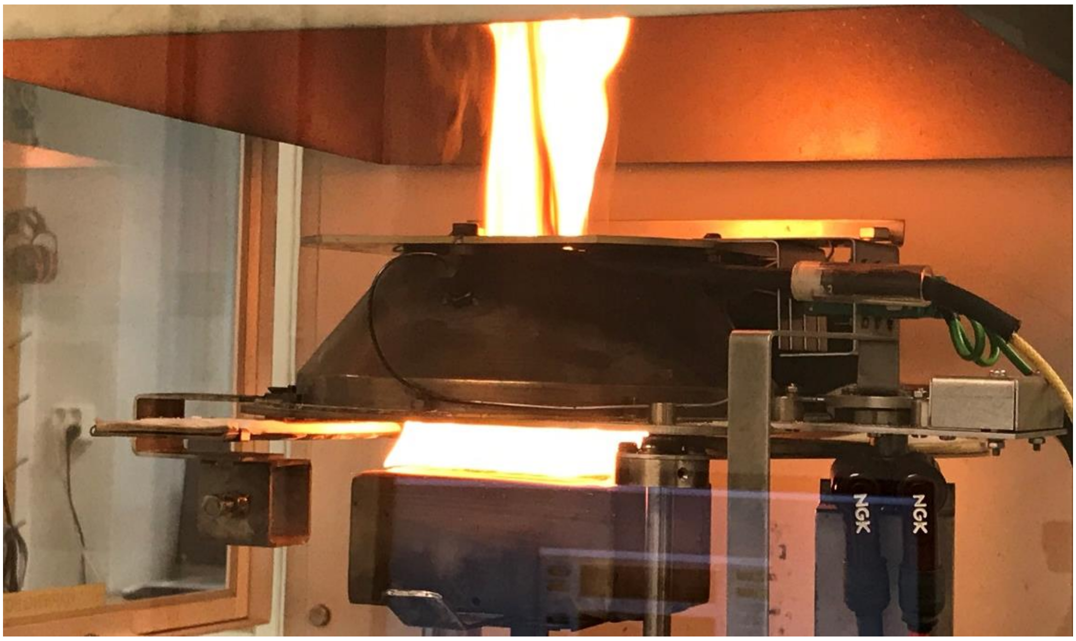


Figure 28 Pure ABS sample burning

Figure 29 Composite sample burning

The changes in burning behaviour of composite samples due to a reduction in oxygen mass fraction have been described based on observations during testing. This behaviour can also be observed through Figure 30 which shows composite samples in ambient conditions as well as 15%O_2 hypoxic conditions and the different production rates of CO_2 and CO of both during the first 150 seconds of testing. The rise in CO_2 represents the point at which flaming ignition commences with the ambient samples observing a higher production of CO_2 because the equivalence ratio is closer to 1 (the process is closer to stoichiometry and therefore less incomplete). The CO_2 production for the hypoxic cases is lower (less efficient burning due to lower oxygen mass fraction). Approximately 20-30 seconds later the CO production for the hypoxic cases rises significantly signifying the start of self-extinguishment of the sample as the available oxygen to complete the flaming combustion is exhausted. This rise in CO is not observed for the samples in ambient conditions as the samples do not self-extinguish and the combustion process continues as the ABS layer reaches its critical heat flux. As previously noted, in hypoxic conditions the reduction in HRRPUA and rise in by-product production causes more of the samples to self-extinguish, and can be observed in Figure 30 as well as the general HRRPUA data. The rise of by-product yields can be seen in CO yield data shown in Figure 31.

Due to the restricted laboratory access one test that has not been conducted but would have given interesting comparison would have been the removal of the bubble wrap layer from the composite sample to examine the effect that the bubble wrap had on the experimental data. Conducting this testing would have given further insight into the impact of the local aerated cavities within the composite sample. Another potential variation in testing which would have provided useful insight into composite material behaviour would have been the examination of vertically orientated composite samples. As the generation of a protective layer on the composite sample was critical to its performance a vertical sample is likely to see entirely unique material performance where the protective layer falls off rather than protecting the ABS layer.

One of the primary conclusions reached from testing composite samples is the need for guidance standards to recommend an increased number of repeat tests for composite samples. The increased number of variables has a clear impact on the range of results collected where compared to pure samples. For example, the development and disruption of the top ashen layer has a significant impact on the remaining data collected in the test.

The composite samples also provide a more conservative indication of the type of fires that ORS systems are exposed to. As noted in Section 2 Part 3 ORS are not capable of providing their contents protection from smouldering fires. The composite samples present a greater opportunity to support smouldering conditions particularly in a horizontal orientation where the top layer pyrolysis protects other composite layers below from direct interaction with the vitiated oxygen atmosphere but provides heat suitable to sustain smouldering.

It is notable that there is a high degree of variability between composite samples particularly where compared to the pure samples tested. This adds challenges to the conclusions made where analysing data as there is no longer a clear trend which subsequently leads to some trepidation in drawing too definitive conclusions. For example, direct comparisons to heat release rates and their absolute quantities between samples becomes an ineffective and inaccurate method of analysis. Due to this exact analysis was avoided in favour of observing general observations. General trends, where all three tests sill observed similar behaviour, or the lack of a trend, allowed for conclusions to be reached.

For example, general conclusions regarding the behaviour between Test 17, where composite samples under hypoxic conditions were observed to produce a higher HRR than in ambient Test 7, could be made because the behaviour of each repeat test was broadly similar. All three of the peak HRRPUA in test 17 were higher than the highest peak HRRPUA in Test 7 which can be confirmed in the graphs found within the Appendices. High level conclusions, such as the increased complexity of composite scenarios, could also be made without being impacted by the variability of composite results.

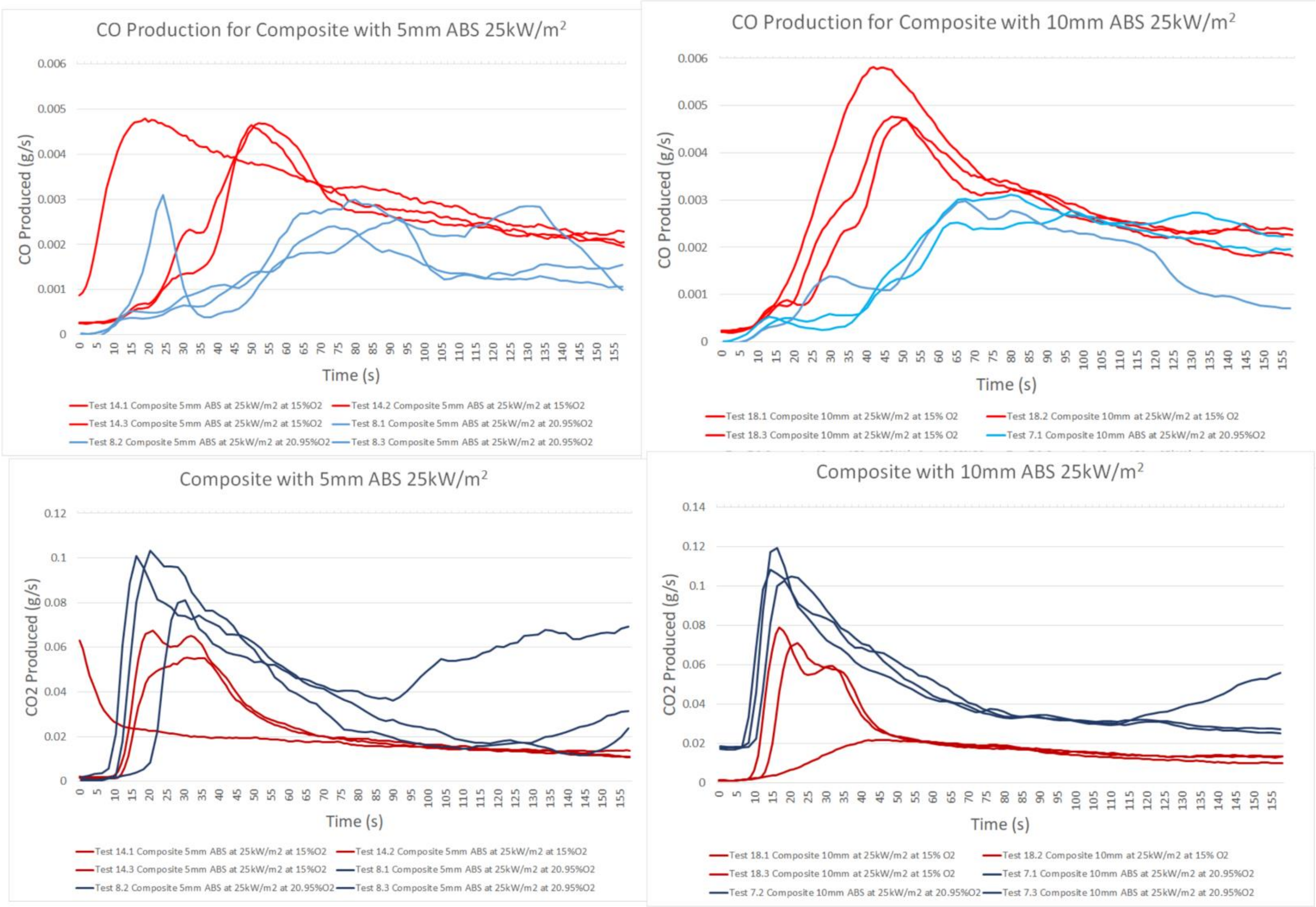


Figure 30 Comparison of CO and CO_2 production rates during initial 150s of tests for 20.95% and 15% O_2 atmospheres

Section 5.4 - Impact of oxygen concentration

Effect of oxygen concentration on ignition times

The irradiance levels effect on time to ignition was not affected by the material thicknesses and was only slightly a function of the oxygen concentration. It is not suggested that material thickness is not an important factor for time to ignition, as highlighted by Nilsson and van Hees (5), material thickness is likely to affect the burning performance in some cases. However, the range of thicknesses tested within the study (5mm to 20mm) were not observed to produce notably different results for ignition times. The arrangement of composite layers was found to be a much more significant factor for ignition times. Regarding the impact of oxygen concentration, there was approximately a 10-30 second delay in sample ignition of ABS at 10mm when the oxygen concentration was reduced from 20.95% to 15%. This appears to be in disagreement with the work of Deliachatsios (43) who concluded that reduced oxygen atmospheres do not affect the critical heat flux, particularly for radiant heat fluxes less than 50kW/m^2. This is perhaps due to the difference in materials tested (ABS rather than 4mm thick plywood) or the experimental setup (changed from a CC to a CACC during testing). The work of Chiti(86) recorded results showing that ignition time is indeed a function of oxygen concentration such that the ignition times were said to increase drastically when the oxygen concentration was below 17%. The materials tested ranged from plastics, paper and wood but the test setup was variable and rather than a spark ignitor a flaming torch was used to ignite samples. Chiti did not impose a heat flux to the samples during testing. In the experiments conducted the change from 17% to 15% oxygen concentration is shown to have a negligible effect on ignition times whereas there is a slight increase in ignition times from 20.95% to 15%. However, the relationship between ignition time and oxygen concentration is weak particularly when compared to the relationship between imposed heat flux and ignition time. It is reasonable therefore to propose that by applying an imposed heat flux to samples one could offset inaccurate test variables for sample size, thickness and composite composition in order to ensure that adequate ORS resilience is assured through a limited number of tests. The range of applicability of increased heat flux in lieu of full-scale sample thicknesses has not been explored further within the scope of this study.

Effect of oxygen concentration on heat release rate and mass loss rates

It has been demonstrated, as shown in Figure 22, that the reduction of oxygen concentration has caused the reduction of maximum values for HRRPUA and MLR with a greater impact observed on thicker samples. The relationship between oxygen concentration, HRRPUA and MLR is more complex for composite samples as previously discussed in Sections 5.1 and 5.3. For pure ABS samples the HRR and MLR data observed similar behaviours due to the co-dependent nature of the phenomena and as would be typically expected in the literature reviewed.

Effect of oxygen concentration on non-ignition and self-extinguishment

It is clear from the results of the study shown in Table 1 that a lower oxygen concentration promotes a reduced likelihood of ignition as well as increase the likelihood of self-extinguishment. Despite this, the tests show that even at 15% O_2 (below the 16%O_2 threshold for ABS in EN16750:2017 and VdS 3527:2018) ignition and reignition of samples is not only possible but also probable. This is likely due to the exposure of the sample to an external heat flux which has been shown to cause a reduction in required ignition threshold (9). Interestingly, samples were shown to be more likely to self-extinguish, or not ignite at all, in composite arrangements and more likely still when the composite arrangement contained a thermally thicker backing layer. The results indicate that non-ignition and self-extinguishment are functions of oxygen concentration and heat flux but the dependency on these factors is not so great that it cannot be influenced by other factors such as thickness and material arrangement.

Effect of oxygen concentration on CO and CO_2 yields

The CO yield of four comparable tests (2 pure ABS and 2 composite samples) at 15%O_2 and 20.95%O_2 are shown in Figure 31. The elevated values for CO yields broadly match the time where flameout data is recorded in Table 1. The 15% oxygen samples clearly show two peaks (initial extinguishment and secondary extinguishment after the spark igniter has been reintroduced). The spread of elevated CO yields seems to be larger in ambient conditions which could be due to the increased influence of ambient conditions and air entrainment into the flaming region. It is theorised that the ambient conditions introduce more fluctuation to CO yields due to the greater reliance that combustion efficiency has on turbulent mixing (compared with hypoxic conditions where there is a lower flame height and more consistent flow rates into the flaming region). The CO yield varies due to the interaction between the fuel and ambient oxygen with higher CO yields where there is a lack of oxygen to fully burn the fuel. On average CO yields are higher in hypoxic conditions which is as expected.

The finding that CO yields were higher under hypoxic conditions is in alignment with the findings of Mulholland et al (15) who found that the yield of CO increased, and the CO_2 decreased when the oxygen concentration was lowered in ABS samples. Mulholland et al found that at 21%O_2 and 20kW/m^2 irradiance the CO yield 0.056g/g which increased to 0.104g/g where the oxygen concentration was reduced to 15.2%. A comparison of the values collected by Mulholland between a few of the similar tests conducted in this study is shown in Table 3.

Source	**Material**	**Irradiance (kW/m^2)**	**O_2 concentration (%)**	**Y_{CO}**	**Y_{CO2}**
Mulholland et al(15)	ABS	20	21	0.056	2.4
Mulholland et al(15)	ABS	20	17	0.087	2.3
Mulholland et al(15)	ABS	20	15.2	0.104	2.0
Test 5.1	ABS	25	21	0.024	**0.88**
Test 5.2	ABS	25	21	0.067	**5.47**
Test 5.3	ABS	25	21	0.010	**0.377**
Test 8.1	Composite	25	21	0.040	**1.453**
Test 13.1	ABS	25	15	0.12	2.21
Test 13.2	ABS	25	15	0.20	2.73
Test 13.3	ABS	25	15	0.11	2.1
Test 14.1	Composite	25	15	0.077	1.455

Table 3 CO_2 and CO yields compared to other data

Most of the tests conducted show similar yields than found in the work of Mulholland et al. The exception to this is the results from the CO_2 yields in ambient conditions which appear to be in error.

The values also indicate that CO yields between pure and composite samples were typically similar. Although data peaks are greater for composite samples the values are in the same order of magnitude. The data seems to suggest that there is not a clear enough trend to indicate a correlation between composite samples and higher CO yields due to the variability in the values collected.

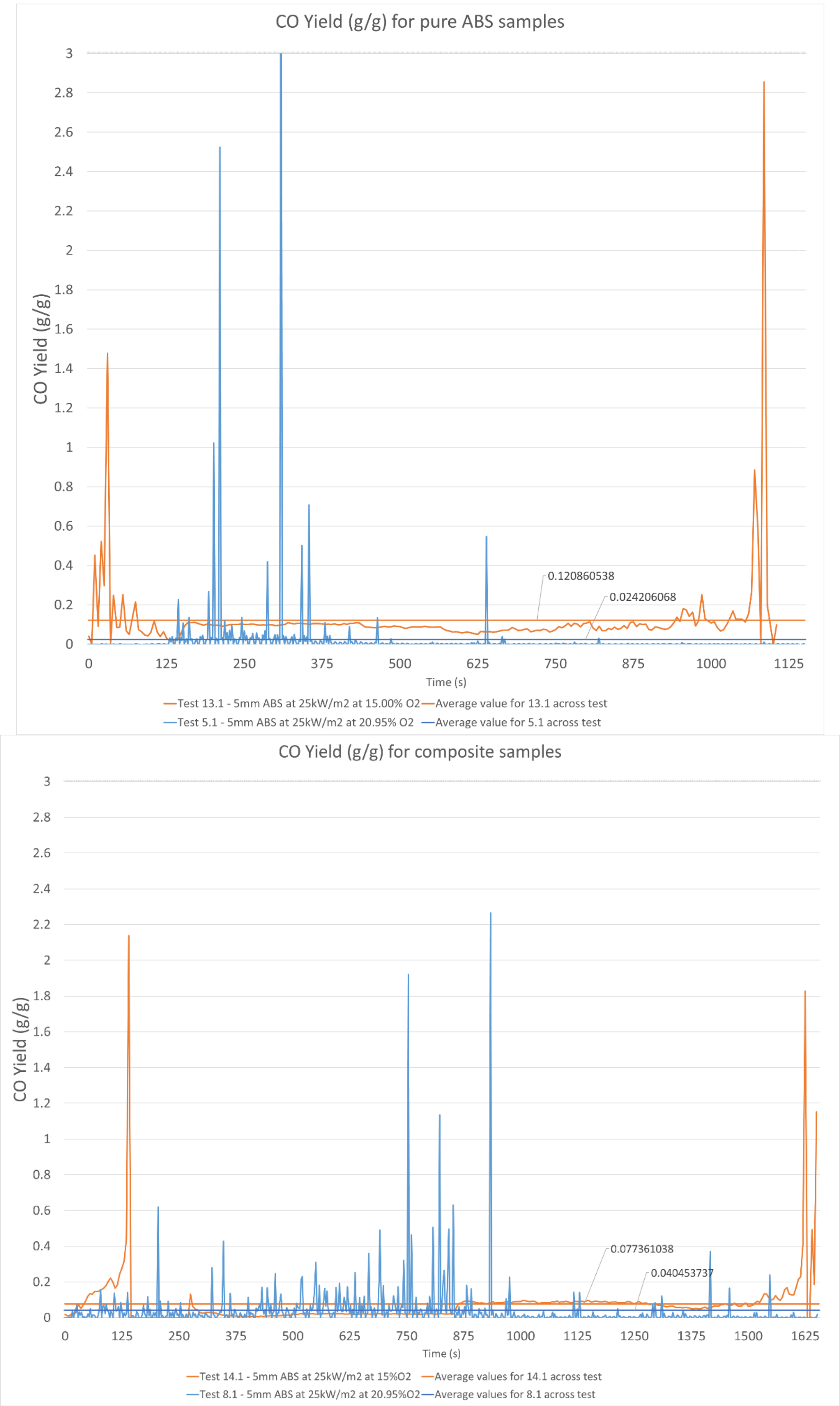


Figure 31 CO yields for composite and pure samples at various O_2 concentrations

Section 6 - Conclusions

The study conducted involved the examination of pure and composite materials under ambient and hypoxic conditions using bench scale testing methods. The intended purpose of the study was to improve the data resource available for composite materials exposed to hypoxic conditions and to examine how this data could be used to enhance current regulatory standards for ORS design (namely EN16750:2017 and VdS 3527:2018). Acrylonitrile butadiene styrene (ABS) samples of various thicknesses (20mm, 10mm and 5mm) have been compared to a composite mix of ABS with a surface layer of cardboard and secondary layer of bubble wrap. Tested materials were considered reasonable because they represent a plastic commonly used in the formation of high-end electronic devices whilst cardboard and bubble wrap layers represent common storage components. The samples were tested with exposure to radiant heat fluxes, namely 25kW/m^2, and 50kW/m^2. The oxygen concentrations compared were 20.95%, 17% and 15%.

The following conclusions were made upon completion of the study;

1. Results indicate that hypoxic conditions have a greater impact on HRRPUA for thermally thicker samples where ABS samples of 10mm and 5mm are compared. It is theorised that this is due to the changing ratio of heat released by flaming combustion to heat losses into the material that is altered by the introduction of hypoxic conditions. Where thermal inertia is higher, and therefore heat losses into the virgin fuel are greater, vitiated conditions are shown to cause a greater reduction of heat released when compared to samples of the same thickness in ambient conditions.

2. The thermal thickness of the underside of composite samples was shown to influence the likelihood of samples to ignite under hypoxic conditions. Composite samples were less likely to ignite or reignite in 10mm composite ABS samples compared to 5mm composite ABS samples because more heat was absorbed by the increased thermal inertia of the underlayer. The impact of thermal thickness was shown to be less significant in pure samples because all pure samples ignited.

3. Material behaviour was shown to change dramatically between hypoxic and ambient conditions, and in completely opposite ways in some cases, between pure and composite samples due to the inclusion of an ash forming top layer. It is argued that material performance under hypoxic conditions cannot be determined by examining material parts independently as material performance is intrinsically linked to the performance of the materials as a collective system.

4. In composite samples the results demonstrated that hypoxic conditions may cause higher heat release rates than for the same arrangement in ambient conditions. The exposure of preheating overcoming material temperature gradients due to delayed reignition, in this case from a combination of the hypoxic environment and behaviour of the composite material tested, was shown to produce greater heat release rate outputs. This identifies a risk for ORS systems because prolonged ignition times, whilst under exposure to a heat source, increases the likelihood of thermal equilibrium within the material. In some instances, it is plausible that hypoxic conditions may lead to worse burning conditions than could be expected in an ambient environment where the ignition threshold is not low enough and significant preheating occurs due to delayed ignition.

5. Due to the complex set of variable conditions introduced from the inclusion of composite materials it has been demonstrated that there is a need for regulatory standards to recommend an increased number of repeat tests for composite samples.

6. The experimental results support the findings of Xin and Khan(9) in noting the importance of irradiance to the value of the ignition threshold. Additionally, it is evident that the thermal thickness and composite arrangement of the ORS contents will also influence the ignition threshold of the tested materials.

7. In some cases, composite materials performed better than pure materials under an imposed heat flux. Where the surface layer decomposed due to the imposed heat flux, before ignition from the spark igniter, it acted to shield the ABS layer below and prevent ignition entirely. If taken based on the materials constituent parts (as per the ORS standards) the composite material would have required a lower ignition threshold (cardboard= 15%O_2 compared to ABS= 16%O_2). However, in this instance the pure material required a lower ignition threshold which again illustrates the oversimplification of considering materials in isolation when determining ignition thresholds for ORS.

Based on the conclusions found during the experimental study the following recommendations are made to the ORS regulatory guidance standards reviewed (EN16750:2017 and VdS 3527:2018);

1. In some cases, testing of true material thicknesses and composite samples is not possible due to the variability of these features over time. As the ignition threshold has been shown to be a function of these variables it is necessary to determine a method of offsetting unknown variations such that a threshold is provided ensuring acceptability regardless. It is concluded, in agreement with van Hees et al(2), that the inclusion of an applied heat flux onto the testing regime of ORS systems would help to ensure an ignition threshold that is not reliant on thermal thickness or composite arrangement. By removing reliance on other variables the testing regime would ensure a more rigorous LOC via a reduced number of required tests.

2. A recommended value for the applied irradiance has not been explored as part of this study. The current study does however provide a warning regarding the use of heat flux as a method of determining ignition threshold. Test data described in Section 5.3 indicates that using irradiance levels that are too great could drastically change burning behaviour, particularly in composite samples, and present misleading results on the sort of burning behaviour anticipated by the material. Where determining an appropriate heat flux to offset thickness and composite variabilities there is a risk that the applied heat flux will invalidate results by changing the anticipated burning behaviour of the sample. If a heat flux is to be imposed, it should be compared to test data where no heat flux is imposed to ensure general burning behaviour is not significantly affected.

3. If a heat flux is not imposed onto materials in the ORS testing regime then more variables should be considered. Where the ORS design includes a composite material arrangement, that is consistent and predictable throughout the room, it should be tested in both vertical and horizontal arrangements. VdS3527: 2018 only mentions the testing of vertical arrangements whilst EN16750: 2017 recommends that the most challenging vertical arrangement is selected. Within the literature review conducted a vertical arrangement was indeed shown to be more suitable for assessing flame spread along a material in hypoxic conditions. However,

the examination of composite samples suggests that materials can be expected to demonstrate significantly different burning behaviour where an ash layer, or potentially charring, forms over the sample. Testing in both horizontal and vertical orientations would, in some instances, be appropriate in ensuring that a greater range of burning outcomes would be explored in hypoxic conditions before assuming an acceptable outcome in composite samples.

4. Both standards currently suggest that each test is conducted three times to ensure acceptability. As demonstrated by the variability of composite data compared to pure plastics there are a much wider range of outcomes. The ORS standards should make note of this and recommend a larger number of repeat tests for composite burning samples.

5. As shown by the samples tested within the current study there is the potential for prolonged exposure to preheating in hypoxic conditions causing an increase in the severity of output data. Both tests for VdS3527: 2018 and EN16750:2017 limit material exposure to the pilot flame to 3 minutes. It has been noted in the tests conducted (Test sets 12 and 14) that delayed ignition can often occur in the samples and that this is more likely in the composite samples tested. Whilst it is recognised that any exposure time is somewhat arbitrary it is evident that, at an exposure time of three minutes, there is limited assessment of prolonged exposure to an ignition source such that the greater resilience of the system is tested.

The imposition of too many repeat tests is likely to be at a detriment to the design of a testing regime of ORS as it would introduce extra cost into the design process. It is therefore proposed that a high heat flux, which would find a more accurate value for LOC as heat losses are no longer a cause of ‘premature’ extinguishment, would reduce the number of required tests whilst also ensuring for a more rigorously determined LOC. Factors such as thickness, orientation, sample size, composite layers, are likely to become less of a factor if an applied heat flux offsets the test reliant variables such that only a single test is necessary.

Section 7 - Future work

The work conducted within the current study had a limited scope due to the imposed time frame and the interruptions caused by Covid-19. Subsequently there are many future directions for further exploration of the topic. These include, but are not limited to;

1. Conducting composite tests in different orientations to confirm a change in material behaviour when tested vertically. As the generation of a protective layer on the composite sample was critical to its performance, a vertical sample is likely to see entirely unique material performance where the protective layer falls off rather than protecting the ABS layer.
2. Reducing and removing composite contents, such as the removal of the bubble wrap layer, to confirm the effect this has on material performance
3. Testing on a larger scale in order to emulate the required conditions for EN16750:2017 and VdS 3527:2018
4. Making use of CFD modelling to replicate material behaviour in hypoxic conditions
5. Examining a wider range of imposed irradiance levels and oxygen concentrations to present a wider range of material behaviours under hypoxic conditions. This would also allow the exploration of to what extent the heat flux must be raised to reduce the impact of thermal thickness on ignition thresholds in hypoxic environments.
6. Examining the impact of changing the ignition source to which the sample is exposed to.

The work conducted as part of this thesis could have been improved, and with hindsight, the following would have been a useful addition to improve it;

1. To save time repeat tests at the same heat flux were run in order. To reduce uncertainty the repeat tests could have been reordered. This would have been time consuming due to the equipment used but would have reduced potential errors replicated between repeat tests.
2. Applying a preheating time of exposure to ambient samples so as to reflect the time that the samples using the controlled atmosphere conditions were exposed to the applied heat flux, used to regain chamber equilibrium, would have removed any additional discrepancy that this caused in the data.
3. Prioritising tests on the composite sample where the bubble wrap is removed would have been useful as it would have allowed for more discussion regarding the impact of the aerated cavity in the tests.

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