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Methodology for Estimating Pyrolysis Rates of Charring Insulation Materials using Experimental Temperature Measurements

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7 Abstract

8 This paper presents the application of a simplified method to estimate pyrolysis rates from rigid closed-cell 9 cellular plastics by means of experimental temperature measurements. These materials are extremely 10 effective in meeting energy efficiency goals in buildings and their safe use should also be enabled and 11 optimised by undertaking comprehensive fire safety analyses. The proposed methodology consists of 12 determining the mass loss as a function of the thermal evolution by applying a mass conversion directly 13 using thermogravimetric data under non-oxidative conditions. In order to verify this simplified method, an 14 experimental programme based on 100 mm thick samples of rigid polyisocyanurate foam was conducted 15 using a Cone Calorimeter, obtaining measurements of mass loss and temperature within the core of the 16 material. A Monel plate was used on top of the sample in order to represent a simpler boundary condition 17 by eliminating the smouldering process of the charred material. Although the pyrolysis rates using this 18 methodology did not provide a perfect fit with experimental data, they showed similar trends, with a slightly 19 delayed prediction but still accurate magnitude. This methodology presents potential for fire safety 20 engineering applications in two domains: (1) as a complementary technique to improve the interpretation 21 of results from standard and ad-hoc testing, and (2) as a design technique for the evaluation of potential 22 heat release contribution and gaseous emissions of assemblies incorporating insulation materials.

23 Keywords

24 Insulation materials; Fire Safety; Pyrolysis; Modelling; Performance-based design; Charring

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25 Nomenclature

k	thermal conductivity $(W \cdot m^{-1} \cdot K^{-1})$
С	specific heat capacity $(J \cdot kg^{-1} \cdot K^{-1})$
f	non-dimensional fraction of remaining mass (-)
i	number of element (-)
j	number of time step (-)
k	number of exposure area (-)
L	thickness (m)
т	mass (g)
'n	mass flow (g·s ⁻¹)
ṁ″	mass loss rate per unit area (g·s ⁻¹ ·m ⁻²)
Ν	maximum number of finite differences (-)
q	heat (W)
t	time (s)
S	surface area (m ⁻²)
Т	temperature (K or °C)
x	distance (m)
Y	yield (g·g ⁻¹)

Greek letters

α	absorptivity/emissivity (-)
ΔH_c	effective heat of combustion $(J \cdot kg^{-1} \cdot K^{-1})$
Δt	time step (s)
Δx	finite difference thickness (m)
ρ	density (kg·m ⁻³)

Subscripts

0	initial
cr	critical
i	of the difference i
net	net/conductive
Р	pyrolysis
Ζ	species

Acronyms

HRR	heat release rate
MLR	mass loss rate
PIR	rigid closed-cell polyisocyanurate foam
SIP	structural insulated panel

TC thermocouple

TGA thermogravimetric analysis

U-value thermal transmittance

26 **1. Introduction**

27 During recent decades sustainability has become one of the main drivers in building construction, 28 resulting in highly thermally efficient buildings. Several techniques may be used to achieve the stringent energy efficiency requirements defined by the Energy Performance of Buildings Directive [1], e.g. thermal 29 30 insulation within the building envelope, increased levels of air tightness, efficient heat recovery of the 31 ventilation systems, reduction of thermal bridging and/or more efficient windows [2]. The intense use of 32 thermal insulation is one of the primary targets due to the large surface area of the building envelope and 33 the architectural aspirations. As a result, low thermal transmittances (U-values) are required, which can 34 only be achieved by significantly increasing the thickness of insulation used.

35 Due to the multi-criteria nature of building design, stringent U-values clash with other desired design 36 criteria such as efficient space usage and cost. Despite the large diversity of insulation materials in the 37 market [3], under this competitive scenario closed-cell plastic foams have become an easy and cost-38 effective solution because of their relatively low thermal conductivity. The most common closed-cell 39 insulation foams at present being used are rigid polyisocyanurate foams, commonly known as PIR, and 40 phenolic foam. These materials are often provided as boards with a foil-facing on the surface and used for 41 framing construction or masonry cavity walls; alternatively they can be embedded directly within linings, 42 e.g. sandwich panels or structural insulated panels (SIPs) [4].

43 Despite the fact that these materials are extremely effective in meeting energy efficiency goals, their use 44 should be also enabled and optimised by undertaking a comprehensive fire safety analysis, i.e. systems 45 including insulation materials should be optimised while still ensuring life safety and property protection.

46 **1.1.** Fire performance of closed-cell plastic insulation materials

47 The fire performance of these materials has been studied by several authors at different scales [5-19]. Generally, these types of plastics are classified either as thermoplastics or thermosets. Thermoplastics (e.g. 48 49 expanded polystyrene) exhibit melting behaviour, while thermosets (e.g. polyisocyanurate or phenolic 50 foam) exhibit a charring behaviour, leaving a carbonaceous residue after pyrolysis. A complete description 51 of the different mechanisms of thermal decomposition for these polymers is described by Witkowski et al. 52 [5]. These mechanisms result in different fire performance, with a charring behaviour being more desirable 53 due to the positive effect of the char layer on the reduction of the pyrolysis rate. Several authors have 54 focussed their research at the material scale (e.g. thermogravimetry), looking at polymer formulations that 55 promote larger residue generation and endothermic reactions in the solid-phase [6–8]. These techniques of

flame retardancy have been largely covered by *Hull and Kandola* [9]. However, the majority of research

57 has focussed on the macroscopic material behaviour using bench-scale testing, thus concentrating on the

ignition mechanism and release of heat from these materials [10–19]. More extensive experimental work

59 covering different scales can be found in references Error! Reference source not found. and Error!

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61 Recently published work showed the relation between the thermal degradation at the material scale 62 linked to the heat transfer phenomena within the solid material [20]. Rigid closed-cell polyisocyanurate and phenolic foam showed similar behaviour, i.e. materials that experience pyrolysis and char formation. The 63 64 char layer reduces the heat transport to the pyrolysis front resulting in a slower propagation and lower 65 pyrolysis rate. Typically, this insulating effect of the surface char layer limits the heating of virgin foam to 66 several degrees per minute. Experimental results showed that this char is however highly vulnerable to 67 surface oxidation (smouldering). The smouldering process was shown not to be self-sustaining due to the large heat losses under the specific experimental conditions. In addition, the closed-cell structure of the 68 69 polymer restricted the air flow through the foam which was shown to be a key factor to limit self-sustaining 70 smouldering [20]. In end-use conditions, the insulation materials are typically covered by a lining or a 71 physical barrier, thus limiting the contact with the air, unless they are introduced in partial fill cavity walls. 72 As a result, this smouldering behaviour is not expected under real fire conditions. Therefore, initially only 73 pyrolysis should be considered as the primary hazardous event.

74 **1.2.** Fire safe design of insulation materials

It has been widely recognised that the organic polymer nature of closed-cell plastic foams may represent a fire risk in buildings [21–23]. The fire safe design of building assemblies including insulation materials has been classically based on a material classification and a pass-fail criteria frameworks, e.g. in the EU represented by the Euroclasses system [24] and the fire-resistance framework [25], respectively. The prescriptive nature of these frameworks however does not allow for a quantitative design to be carried out on the basis of the specific insulation fire hazards, and as a result it is not possible to quantify the associated fire risk [26].

Previous work demonstrated that the initiating hazard from this type of insulation material corresponds to the onset of pyrolysis [26]. After this is achieved, there is potential for the generation of a large amount of flammable gases that may be transported to the compartment fire, or alternatively may escape to areas away from the fire enclosure. The former may represent an increase in the heat release rate of the fire, while the latter may represent a life safety hazard for the occupants of the building due to the intrinsic toxicity of the pyrolysis effluent. Current mitigation practices are thus based on the design of suitable thermal barriers
that delay or cancel the onset of pyrolysis of the insulation material [27].

89 Whilst the previous approach stands out by its simplicity, which is easily achievable in engineering 90 terms, it may be very conservative for some scenarios. A more accurate approach should rely on estimating 91 the rates of pyrolysis from the insulation under specific fire scenarios. By determining the pyrolysis 92 behaviour, the evolution of the hazard (potential contribution to the fire and generation of toxic species) 93 can be quantified [28]. This approach requires a pyrolysis model which is able to accurately predict the 94 thermal behaviour of the insulation. In the last decade, such pyrolysis models have been developed and 95 validated [29–32]. These models tend to require a large number of parameters that are often unknown, 96 necessitating inverse modelling techniques that can introduce significant compensation errors [33] and 97 demand a great deal of expertise. An additional handicap on the use of these tools is that the thermal 98 boundary condition under real fire scenarios is difficult to quantify. Consequently, if pyrolysis rates are to 99 be quantified at an appropriate level for engineering design optimisation, simpler approaches are necessary.

100 1.3. Research aim

101 This work aims to assess the applicability of a simplified methodology for quantifying pyrolysis rates 102 and temperature evolution from foil-lined closed-cell charring insulation materials under severe conditions 103 of heat exposure. It focusses on small-scale experiments so as to reduce the uncertainty in the assessment, thus precisely controlling the thermal evolution and mass loss of samples under a heating regime that is 104 105 close to one-dimensional. Despite the fact that characterising the pyrolysis represents a challenge due to the 106 large number of material properties to be quantified, the presented simplified experimental approach still 107 allows prediction of the hazard while keeping the method simple. The success of this approach will allow 108 estimation of pyrolysis rates from this type of insulation in research-driven large-scale experiments and 109 standard testing. Given that the pyrolysis rate represents the main physical variable determining the heat 110 release contribution and yields of toxic species, the application of this methodology will help to improve 111 current testing practices.

112 **2. Experimental programme description**

The experimental programme was designed to explore the applicability of simpler modelling approaches, and based on the use of the Cone Calorimeter apparatus [34] and thermogravimetric experiments. The Cone Calorimeter set-up was modified to remove the pilot spark and to enable heating of the sample by conduction from a metallic plate on the exposed surface. The main measurements consisted of mass loss and temperature within the samples, supported by visual observations. Four experiments were performed for each thermal exposure, two repetitions measuring only mass loss, and two repetitions taking temperature measurements within the samples. The thermogravimetric data corresponded to thosepresented by the authors elsewhere [35].

121 **2.1.** *Materials*

The studied insulation material corresponded to a type of rigid polyisocyanurate foam previously 122 described as PIRb elsewhere [20,35]. Samples with a surface area of 90 mm by 90 mm and 100 mm thick 123 124 were tested for this series of experiments. The metallic plate as boundary element at the surface of the 125 samples corresponded to a 6 mm Monel plate, painted with a high temperature optical black coating of 126 known absorptivity ($\alpha = 0.92$, Medtherm Corporation®). The use of the plate presents a case study 127 representative of a common end-use condition of insulation materials, as these are rarely installed 128 uncovered but behind a lining. The oxidation rate is expected to be reduced or eliminated by using this 129 methodology, therefore also reducing the complexity introduced by the smouldering process for future 130 modelling purposes. A metallic plate (6 mm thick, Nickel 200) was used at the bottom of the sample as a 131 heat sink. A sample with the protective foil layer removed and prepared for testing with the metallic plates 132 on top and bottom is shown in Figure 1a.



133

134Figure 1. (a) PIR sample prepared for testing. (b) PIR sample wrapped in aluminium foil and ceramic paper135with metallic plates and thermocouples inserted into the centre of the sample through ceramic tubes. A136special holder was designed to keep the thermocouple horizontal during the insertion.

137 2.2. Experimental set-up

The samples were wrapped with aluminium foil on the bottom and lateral sides, with the 6 mm Monel plate placed on the top and the 6mm Nickel 200 block at the bottom. Sample and plates were wrapped in two 3 mm thick layers of ceramic insulation paper. The purpose of the aluminium foil was to prevent air penetration into the sample from the sides, as the ceramic paper is a porous element, to promote one dimensional pyrolysis. The real set-up and a schematic drawing of this are shown in Figure 1b and Figure 2.





145

Figure 2. Schematics of sample preparation.

In order to provide a well-characterised experimental set-up to allow modelling to be undertaken, the characterisation of the boundary condition at the back face of the material was achieved by using the 6 mm Nickel 200 plate at the bottom of the samples. This approach was described by *Carvel et al.* [36], who recommended the use of a heat sink for material characterisation purposes. Using a metallic plate on top would act as a dummy surface temperature sensor, although contact resistance effects may induce a thermal gradient between sample and metallic plate. This is discussed in subsequent sections.

152 Several levels of irradiation from the radiant heater were used (25, 45 and 65 kW·m⁻²). The heat fluxes 153 were selected such that different rates of pyrolysis would be achieved. Measurements of temperature were 154 taken within the sample by using 1 mm bead N-type thermocouples. The temperature of the metallic plates 155 on the top and bottom was also measured, but with 1.5 mm bead K-type thermocouples. Thermocouples 156 were installed at various depths at the centre of the section (1, 10, 20, 30, 40, 60, 80 mm) parallel to the 157 exposed surface to reduce the error in the thermocouple reading, which is recommended for materials of 158 particularly low conductivity [37,38]. Ceramic tubes were used to insert the thermocouple into the sample, 159 so as to secure the location of the thermocouple for multiple experiments. Additionally, the exact location 160 of the thermocouples could be visually identified after testing. No temperature correction was considered 161 by the heat losses introduced by the thermocouple. The positioning of the thermocouples is shown in Figure 2. A summary of the conditions for all the performed experiments is presented in Table 1. 162

Material characteristics	Configuration	Incident radiant heat flux range /kW·m ⁻²	Measured parameters
	Nominal sample size: 90mm x 90mm x 100mm		
PIRb	Top boundary condition:		
Manufacturer-claimed	Monel 400 plate (6mm)		
density:	Wrapping:	25, 45, 65 (4 repetitions)	 (1) Mass loss (2 repetitions) (2) In-depth temperature (2 repetitions)
32 kg·m ⁻³	2 layers of ceramic paper + 1 layer of		
Average measured	aluminium foil		
density: 22.0 \pm 0.71 km m ⁻³	Back boundary condition:		
55.0 ± 0.71 kg·m ²	Nickel 200 plate (6mm) + Ceramic		
Estimated thermal	board (25mm)		
$6.5 \cdot 10^3 W^2 \cdot s \cdot K^{-2} \cdot m^{-4}$	Orientation:		
[27]	Horizontal		
	Pilot:		
	No pilot igniter		

163 Table 1. Summary of performed experiments

164 **3. Experimental results and discussion**

165 Figure 3a shows the normalised mass for PIR samples with a Monel plate on top under three constant 166 levels of irradiation (25, 45 and 65 kW·m⁻²). The normalised mass is obtained by dividing the mass of the 167 sample at any time by the initial mass (m_0) . Vertical dashed lines indicate the time at which the effluent of 168 pyrolysis gases through the edge of the sample auto-ignited. Results from duplicates show good agreement, 169 with the major discrepancies observed for the highest heat flux after ignition is observed. This inconsistency 170 in the results is however expected due to the behaviour of the pyrolysis effluent for each experiment, 171 resulting in extra heating of the surface metallic plate when ignited. The sample residue obtained after 1800 s of a heat exposure of 25, 45 and 65 kW·m⁻² is approximately 88%, 75% and 60%, respectively. 172

173 Figure 3b shows the mass loss rate (MLR) per unit area corresponding to the mass loss presented in 174 Figure 3a. The shape obtained for the three heat fluxes is qualitatively similar, with a MLR peak followed 175 by a decay, as characteristic of charring materials [39]. The MLR peak increases in magnitude and shifts to lower times with increasing heat fluxes. Peaks of MLR for 25, 45 and 65 kW·m⁻² are approximately in the 176 range 0.4-0.5, 1.0-1.2 and 2.0-2.4 g·m⁻²·s⁻¹, respectively. Considering a heat of combustion for the pyrolysis 177 gases of 13.22 kJ·g⁻¹ as presented by *Hidalgo* [35], the heat release rate per unit area of these peaks 178 179 correspond to 6.6, 15.9 and 31.7 kW·m⁻², which are fairly moderate values. Therefore, a significant 180 contribution to the heat release in a compartment fire from the insulation is only to be expected if a large 181 surface area is exposed and this is limited to the early stages.



182

Figure 3. (a) Normalised mass for experiments at 25, 45 and 65 kW·m⁻². Vertical dashed lines indicate the auto-ignition of the pyrolysis effluent. (b) Mass loss rate per unit area.

The sample residues for experiments shown in Figure 3 are presented in Figure 4, with a cut through the centre-section. The sample sections show three different regions of discoloration corresponding to the char after pyrolysis (carbonaceous region), reaction zone where pyrolysis process is ongoing (orange region), and virgin material (light yellow/grey region). The regions of discolouration are fairly uniform along the width of the sample, indicating a heating regime similar to 1D. This uniformity is less clear in Figure 4a, corresponding to the sample tested at 25 kW·m⁻². These residues are coupled with the temperature profile during the quasi-steady³ state after 1800 s, obtained from experiments using thermocouples. It should be

³ The term "quasi-steady state" used throughout this paper refers to the stage in which the rate of temperature increase within some sections of the sample is sufficiently low that the net heat flux at the sample surface has achieved an asymptotic behaviour, close to a constant heat flux that defines a steady conduction.

- 192 noted that the temperature measurements are presented as the original locations in the sample before testing.
- 193 The samples tested at 25, 45 and 65 kW·m⁻² presented a shrinkage after 1800 s of about 0, 5 and 10 mm,
- 194 respectively. For ease in the visualisation, the image of the residue has been adapted to the original sample
- size of 100 mm to fit into the same scale of the temperature-depth diagrams.



197Figure 4. PIR residue after 1800 s of heat exposure of (a) 25, (b) 45 and (c) 65 kW·m-2. The maximum198temperature achieved for each depth is presented on top of each cut presented as background.

Figure 5 shows the temperature measurements obtained for experiments with thermocouples under 25, 45 and 65 kW·m⁻². Duplicated experiments are shown as dashed lines. In general, good repeatability is obtained for experiments at 25 and 45 kW·m⁻², while for 65 kW·m⁻² this is not that good for thermocouples in the 10 mm and 20 mm in-depth position during the transient state, and also for the top plate. The temperature at the top plate experiences a sudden increase due to the auto-ignition of the pyrolysis effluent. Then, the temperature decreases significantly, with a noisy reading, thus indicating a bad contact between thermocouple and plate, which was later corrected.

206 The readings presented in Figure 5 indicate a clear effect of the contact resistance during the 207 experiments. During the transient state the temperature difference between plate and first position within 208 the sample (1 mm) is clearly noticeable with a difference of up to 200 °C. However, once the quasi-steady 209 state is reached, the difference drops to only 20 °C. This is a reasonable result, as the net heat flux through 210 the surface of the sample is large during the transient state, reducing continuously until the quasi-steady 211 state is reached. Given a constant thermal resistance of the contact, a larger heat flux will result in larger 212 temperature gradients. While these considerations about the contact resistance are important for heat 213 transfer modelling, for the present analysis they have few implications as a reading near the surface is also 214 available.

215 Additionally, the obtained measurements indicate that the smouldering process has been successfully 216 mitigated by using the metallic plate and aluminium foil, as the temperature evolution follows the trend of 217 an apparently inert solid under a constant irradiation level and heat losses. The critical temperature proposed 218 by Hidalgo et al. [27] for this material (PIR) is 300 °C, which fundamentally represents the onset of hazard 219 (pyrolysis) and corresponds to the primary failure criterion to be considered for the fire safe design of 220 assemblies including insulation. This value is plotted as a horizontal line, showing that samples exposed to 25, 45 and 65 kW·m⁻² achieve the critical temperature at the 1 mm in-depth thermocouple at about 520, 285 221 and 220 s, respectively. These times slightly correspond to the period prior to the maximum increase in 222 223 MLR before the peak, thus validating the conservative definition of critical temperature for charring 224 materials proposed by *Hidalgo et al.* [27].

Figure 6 (solid lines) shows the propagation of the front at 300 °C (assumed to correspond to the pyrolysis front) obtained for the three cases presented in Figure 5 by interpolating the temperature profile for each position. Due to the imprecise positioning of some thermocouples and/or density of temperature measurements within the insulation core, it is observed that the position versus time presents a change of curvature, which otherwise would not be expected e.g. at 500 s, 20 mm depth during the 45 kW·m⁻² heat exposure. Complementary to this, the first derivative of this function that represents the spread rate of the front at 300°C is plotted as a dashed line. A maximum spread rate of 2, 5 and 6 mm·min⁻¹ is observed for

- 232 25, 45 and 65 kW·m⁻², respectively. Consistent with the data of normalised mass, the spread of the pyrolysis
- 233 front experiences an attenuation/decay due to the charring nature of the foam, which is fundamentally a
- consequence of a reducing net heat flux at the pyrolysis front. The fact that the char layer is protected by
- the metallic plate, and therefore not consumed by oxidation, allows the net heat flux at the pyrolysis front
- to keep decreasing as this progresses in-depth.





Figure 6. Position of the front at 300 °C (solid lines) and spread rate of this front (dashed lines) for experiments at 25, 45 and 65 kW·m⁻². Interpolated values computed based on data presented in Figure 5.

244 **4. Modelling analysis**

245 **4.1.** Principles for the simplified pyrolysis rate assessment

246 The simplified pyrolysis model is based on the approach already proposed by *Hidalgo et al.* [40]. This 247 approach consists of a two-step decoupled analysis, first solving the heat transfer problem and then followed 248 by the estimation of remaining mass and pyrolysis rates. Despite the fact that effective thermal properties 249 could be obtained to characterise the PIR thermal evolution, in this work modifications are made and the 250 first step is bypassed experimentally without having to solve the diffusion heat transfer within the solid-251 phase. The approach then consists in determining the mass loss as a function of the thermal evolution. The 252 sample is considered as the space domain x = L (m) divided into N finite differences of thickness Δx_i 253 (m), with i each of the finite differences. As for the analysis in the previous section, the temperature 254 evolution for each finite difference is obtained by linear interpolation. Given that the method is also 255 discretised in time, each time step is defined as j and considered as Δt (s). Then, the normalised sample 256 mass for the time step i is obtained as the following expression representing an integration over the space 257 domain:

$$\bar{m}^{j} = \frac{\sum_{i=1}^{N} \left(\bar{m}_{i}^{j} \cdot \Delta x_{i} \right)}{L} \tag{1}$$

where \overline{m}_i^j is the normalised mass of the finite difference *i*, which is approximated directly as a function of the temperature f(T):

$$\overline{m}_i^j = f(T) \tag{2}$$

The function f(T) establishes the fraction of remaining mass as a function of the temperature in that 260 finite difference, varying from 0 to 1. To simplify this function and remove uncertainty associated with 261 262 fitting of Arrhenius parameters, which depend on the temperature and the concentration/diffusion of oxygen [41,42], f(T) is defined by direct reference to TGA results under sufficiently low heating rates. The TGA 263 264 curves presented in Figure 7 correspond to PIR from the same manufacturer obtained in a non-oxidative 265 atmosphere and heating rates of 2.5 and 20 °C·min⁻¹ [4]. The normalised mass loss rate can be obtained by 266 deriving the mass loss over time, which in a discretised form corresponds to the increment of the normalised 267 mass between time steps divided by the time step. The mass loss rate per unit area can then be calculated by considering the density of the virgin material ρ_0 (kg·m⁻³) and the thickness of the sample L (m): 268

$$\dot{m}_P^{\prime\prime j} = \rho_0 \cdot L \cdot \frac{\overline{m}^{j-1} - \overline{m}^j}{\Delta t} \tag{3}$$

where $\dot{m}_{P}^{\prime\prime j}$ is the mass loss rate per unit area (kg·m⁻²·s⁻¹), or equivalently the rate of pyrolysis per unit area because no oxidation is considered.





Figure 7. Normalised mass of PIR from the same manufacturer obtained by thermogravimetry under a nitrogen atmosphere at 2.5 and 20°C·min⁻¹ [4].

274 **4.2. Results**

Figure 8 shows the experimental and modelled normalised mass loss rate considering the temperature profiles presented in Figure 5. Normalised values of mass loss rate are compared so that the error due to inaccuracy in the dimensions, and therefore density calculation for the modelled MLR, can be minimised. The experimental normalised MLR is obtained by differentiating the normalised mass curves with respect to time (as shown in Figure 3a), while the modelled MLR is obtained by integrating the f(T) function for the whole thickness for each time step as shown in Eq. 1 and 2, and then differentiating with respect to time.

282 It is observed that the model does not produce a perfect fit with the experimental data. This is however 283 not surprising due to the deliberate simplicity of the proposed approach. Nevertheless, it is clear that the 284 primary mechanisms that characterise the pyrolysis from PIR under different heating scenarios are fairly 285 represented, since the results follow similar trends. The most obvious inaccuracy presented by the model is the delay between experimental and model results. This could be partially attributed to a bad adjustment of 286 287 the time lines for experiments with and without thermocouples. Other factors that could contribute to this delay are an insufficiently high density of thermocouples near the surface of the material and/or the linear 288 289 interpolation method. The transport time of the pyrolysis gases could also be a factor, although the time 290 scale is expected to be much lower, of the order of seconds. In any case this is a drawback that can be easily 291 corrected and/or calibrated without affecting the outcomes of the assessment.

292 Another clear conclusion from the results presented in Figure 8 is that the TGA curve for which the 293 model better predicts the experimental results is the one with the highest heating rate used, i.e. 20 °C·min⁻ 294 ¹. Figure 9 shows the heating rate experienced for various locations (1 and 4 mm) at 25 and 65 kW·m⁻². The derived maximum heating rate is around 140 °C·min⁻¹, while for other regions and heat fluxes the heating 295 296 rate does not go over 60 °C·min⁻¹. The slight overestimation of the modelled MLR is consistent with these results, as 20 °C·min⁻¹ is not as high as the heating experienced at certain locations. However, the observed 297 298 heating is obviously not constant, with expected average values closer to the 20 °C·min⁻¹ threshold. Despite 299 the fact that using this heating rate as input for the function f(T) may lead to a slight overestimation of 300 results, in engineering practice this could still be a conservative and practical approach. As a matter of fact, 301 the results using a lower heating rate do not show significantly large overestimations.

Figure 8c shows that the model based on the data from one of the repetitions with thermocouples at 65 kW·m⁻² presents a clear and more significant overestimation of the MLR. This is probably mainly due to inaccurate positioning of the thermocouples for this particular experiment, which did not use a stiffening system as presented in Figure 1b. This highlights the importance of the position and density of temperature measurements in practice.



Figure 8. Experimental and modelling results for (a) 25, (b) 45, and (c) 65 kW·m⁻². Experimental curve corresponds to the average between two repetitions, and the shading is the maximum deviation from repetitions to the average.





314 **4.3.** *Limitations and model uncertainties*

315 **Oxidative conditions**

The proposed model is based on the assumption that no smouldering occurs. Therefore, the applicability of this approach is only valid for non-permeable materials that do not allow oxygen transfer through the matrix, thus the thermal decomposition corresponds to non-oxidative conditions as presented in Figure 7. If oxidative conditions are produced on the top, exposed surface, the calculated rate of pyrolysis is expected to still be reasonably reproduced, however the total mass loss rate would be under-predicted as the char oxidation would be neglected.

The shrinking behaviour of the material would lead to the creation of a gap between lining and insulation. Once this is achieved, air flow may be expected within the gap. After this has occurred the smouldering process may become a relevant hazardous event that would increase the heat flow through the insulation reaction zone.

326 Heating rate

327 While it is normally admitted that the heating experienced by burning fuels is much larger than heating 328 rates obtained by thermogravimetry [43], this is clearly not the case for charring materials such as PIR. The 329 effectiveness of the approach then resides in the low and reducing heating rates experienced by the reaction 330 and virgin zones, as shown in Figure 9. The results presented in the previous section indicate that a heating 331 rate of 20 °C·min⁻¹ provides a reasonable accuracy for all the heating scenarios studied and the particular 332 thickness of 100 mm. The trend in Figure 8 indicates that increased heating rates could provide better results, since 20 °C·min⁻¹ is a heating rate lower than those observed in Figure 9 during the peaks of MLR; 333 334 however the improvement appears to be not very substantial.

335 Thermal interpolation

336 As shown in Figure 8c, an accurate position of the thermocouples and their spacing is essential to 337 obtaining sensible results. For the present case of 100 mm thick samples, 10 mm spacing for regions near 338 the surface and 20 mm for regions far from the surface are able to provide sufficiently good results. While 339 smaller spacing may result in greater accuracy, a system to secure the thermocouple as presented in this experimental programme seems essential, as the error in spacing can easily be of order ± 3 mm when 340 341 thermocouples are inserted without a stiffening system, due to the friable nature of the foam. In addition, 342 the thermal mass of an increased number of thermocouples may result in a 'heat sink' effect, leading to 343 premature quenching of the reaction.

The interpolation method used to obtain thermal evolution between thermocouple measurements was linear. The accuracy of this approach is proportional to the density of thermocouples. Despite the simplicity of the approach, it seems to provide accurate results.

347 Heat transfer dimensionality

The accuracy of the results from this experimental programme also depend on the one-dimensionality of the heat transfer. Observations of the colour change of the experimental sample residues qualitatively indicates that the 1D assumption seems to be fairly correct. While this could be an issue for the presented experimental programme, since the wrapping material had higher conductivity than the samples, in real scenarios however this assumption is rather controlled by the uniformity of the heating boundary condition. For that case, the accuracy would then be limited by the density of measuring points over the surface area of the building assembly being studied.

355

5. Applicability for fire safety engineering

Since the primary fire hazard from these types of insulation can be associated to the pyrolysis process, the main parameter to be quantified is the rate of pyrolysis gas release. Despite the fact that there is large uncertainty with regard to the location, conditions and instant at which these will ignite, due to, for instance, the ventilation conditions of the construction system, the conservative approach is to assume that these would instantaneously contribute to the fire. This way the risk can be quantified more easily.

The presented method, although not extremely accurate, presents a reasonable level of precision for engineering purposes where the degree of uncertainty in other parameters is already high. Two clear applications can be found for the present model as: (1) pyrolysis estimation for fire testing such as largescale experiments or standard testing, and (2) for quantitative design purposes.

366 5.1. Model testing

367 The presented simplified method can be used to develop a model of the pyrolysis behaviour under well-368 defined testing conditions. The concept consists of running ad-hoc and/or standard fire testing including a series of thermocouples to allow an *a posteriori* quantification of the pyrolysis behaviour from the 369 370 insulation. This approach would also allow quantification of the effectiveness of various protection systems, 371 to allow an optimised design solution to be generated. The provision of pyrolysis predictions can 372 complement heat release rate calculations and measurements of gas species from the generated smoke. 373 Within this scope, error bars need to be acknowledged, based on the model limitations and testing conditions 374 noted previously. Clearly, if consistent data are used, expected errors can be quantified and delimited. The 375 potential of this approach resides in the low-cost solution for improved product development, thus reducing 376 costly research based on full-scale testing.

377 5.2. Hazard quantification

The proposed methodology can lead to evaluation of designs, by which the fire hazard from insulation materials can be quantified explicitly if a series of assumptions and hypotheses are established. A diagram describing the application of the methodology for design purposes is presented in Figure 10. The approach consists of evaluating the time to achieve a potential hazardous heat release contribution and gaseous emissions from the insulation.

383 The first step is based on the definition of effective thermal properties and initial thickness for lining 384 and insulation. Then, a series of fire scenarios defined as the conditions of heat exposure (thermal boundary 385 conditions), their respective area of exposure, and exposure time have to be proposed. Next, the thermal 386 evolution of the system lining-insulation has to be estimated for each boundary condition by using a heat 387 transfer solver. For simplicity, the problem can be simplified as a one-dimensional problem and a perfect 388 contact can be assumed between insulation and lining, which are conservative assumptions. At this stage 389 practitioners can either apply the simplified methodology based on a critical temperature proposed 390 elsewhere [26], or alternatively apply the uncoupled pyrolysis model presented in previous sections in order 391 to estimate the pyrolysis rate for each area of exposure. If the former is applied, the failure time of the 392 insulation system is defined as the time when the insulation reaches the critical temperature at the surface. 393 If the latter is applied, a total rate of pyrolysis gas generation needs to be calculated as the sum from each 394 of the exposure areas. The potential heat release contribution can be obtained by multiplying the generation 395 rate by the corresponding effective heat of combustion, while analogously the potential gaseous emissions 396 can be obtained by multiplying by the corresponding yields. The failure time then can be defined as the 397 time to reach a critical value of HRR or emission concentration.

While the calculation of gaseous emissions represents an ambitious task, as these strongly depend on conditions such as oxygen concentration and temperature [44], a series of hypotheses can be set if further toxicity assessments are pursued. For instance, these values can be used as inputs for CFD modelling in order to estimate fractional effective concentrations/doses for tenability assessments [45]. Similarly, potential HRR contributions can be used for tenability assessments in fire (zone/CFD) models.

The potential of this approach resides in the fact that the data required to develop these quantifications can be obtained by using bench-scale tests (for instance, thermogravimetric data or material properties such as thermal properties, yields or heat of combustion) that are often readily available from manufacturers, or by using values presented in the literature.



411 **6. Conclusions and future work**

This paper has presented the application of a simplified methodology to estimate pyrolysis rates from charring insulation materials such as rigid polyisocyanurate foam based on experimental temperature measurements. In order to verify the proposed method, an experimental programme consisting of 100 mm thick samples of rigid polyisocyanurate foam was conducted using a Cone Calorimeter, obtaining measurements of mass loss and temperature within the core of the material. A Monel plate was used on top of the sample in order to represent a simpler boundary condition by eliminating the smouldering process of the charred material.

419 The proposed approach, although not showing a perfect fit with experimental data, has been proved to 420 provide a reasonably good prediction of the pyrolysis rate from a rigid closed-cell polyisocyanurate foam 421 under different scenarios of heat exposure using constant levels of irradiation (25, 45 and 65 kW·m⁻²), and 422 a sample thickness of 100 mm. The simplified methodology is based on the direct use of TGA data to obtain 423 mass loss measurements relying on temperature readings. Since this methodology is limited to non-424 oxidative conditions, the method must be applied for configurations where the insulation is covered by a 425 lining or barrier. The use of TGA data with a heating rate of 20 °C·min⁻¹ and under a non-oxidative 426 atmosphere has been shown to provide a good accuracy, with a slight overestimation in the modelled 427 normalised mass loss rate. The position and density of temperature measurements has been highlighted to 428 be one of the most important factors for achieving accurate results.

429 The presented method presents a reasonable level of precision for engineering purposes where the degree 430 of uncertainty in other parameters is already high. This approach presents potential for fire safety 431 engineering applications in two domains: (1) as a complementary technique to improve the interpretation 432 of results from standard and ad-hoc testing, and (2) as a design technique for the evaluation of potential 433 heat release contribution and gaseous emissions of assemblies incorporating insulation materials. The 434 former approach can be used to allow a better characterisation of the fire performance of the insulation, 435 without the necessity of developing complex numerical models. The latter approach can be used to evaluate 436 designs by which the fire hazard from insulation materials can be quantified explicitly.

Since the approach presented in this paper is limited to experimental measurements of temperature, it may be insufficient for general design purposes, as it is scenario dependent. The main potential of the proposed methodology is that it would allow faster and more effective product development, thus reducing costly research based on full-scale testing. Therefore, future work should focus on determining effective thermal properties that could reproduce the thermal behaviour of the material and treat the problem as a

- 442 two-step uncoupled analysis, as shown elsewhere [40]. The experimental work presented within this paper
- 443 can further be used for the determination of these effective model parameters.

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448 **References**

- 449[1]Directive 2010/31/EU of the European Parliament and of the Council of 19 May 2010 on the450energy performance of buildings (recast), 2010. doi:doi:10.3000/17252555.L_2010.153.eng.
- 451 [2] C. Despret, M. Economidoe, N. Griffiths, J. Maio, I. Nolte, O. Rapf, eds., Principles for 452 nearly zero-energy buildings, paving the way for effective implementation of policy 453 requirements, Buildings Performance Institute Europe, 2011.
 454 http://bpie.eu/documents/BPIE/publications/LR_nZEB study.pdf.
- 455 [3] A.M. Papadopoulos, State of the art in thermal insulation materials and aims for future 456 developments, Energy Build. 37 (2005) 77–86. doi:10.1016/j.enbuild.2004.05.006.
- 457 [4] J.P. Hidalgo-Medina, Performance-based methodology for the fire safe design of insulation
 458 materials in energy efficient buildings, University of Edinburgh, 2015.
 459 http://hdl.handle.net/1842/10601.
- 460 [5] A. Witkowski, A.A. Stec, R.T. Hull, Thermal Decomposition of Polymeric Materials, in:
 461 SFPE Handb. Fire Prot. Eng., 5th ed., Springer, 2016: pp. 167–254. doi:10.1007/978-1-4939462 2565-0.
- [6] C. Dick, E. Dominguez-Rosado, B. Eling, J.J. Liggat, C.I. Lindsay, S.C. Martin, M.H.
 Mohammed, G. Seeley, C. Snape, The flammability of urethane-modified
 polyisocyanurates and its relationship to thermal degradation chemistry, Polymer
 (Guildf). 42 (2001) 913–923. doi:10.1016/S0032-3861(00)00470-5.
- E. Dominguez-Rosado, J.J. Liggat, C.E. Snape, B. Eling, J. Pichtel, Thermal degradation of
 urethane modified polyisocyanurate foams based on aliphatic and aromatic polyester
 polyol, Polym. Degrad. Stab. 78 (2002) 1–5. doi:10.1016/S0141-3910(02)00086-1.
- I. Vitkauskiene, R. Makuška, U. Stirna, U. Cabulis, Thermal properties of polyurethanepolyisocyanurate foams based on poly(ethylene terephthalate) waste, Medziagotyra. 17
 (2011) 249–253. doi:10.5755/j01.ms.17.3.588.
- [9] N. Cinausero, B. Howell, G. Schmaucks, G. Marosi, Z. Brzozwski, J.-M.L. Cuesta, G.
 Nelson, G. Camino, C. Wilkie, A. Fina, J. Hao, S. Nazare, E. Kandore, J. Staggs, Y.C. Wang,
 S. Duquesne, R. Hicklin, P. Wakelyn, S. Gaan, A.R. Horrocks, P. Joseph, D. Purser, A. Stec,
 M. Hassan, C. Kindness, B.B. Marosfoi, T.R. Hull, B.K. Kandola, Fire retardancy of

- 477 polymers: new strategies and mechanisms, The Royal Society of Chemistry, 2009.
 478 doi:10.1039/9781847559210.
- 479 [10] K.T. Paul, Burning characteristics of materials, Fire Mater. 3 (1979) 223–231.
 480 doi:10.1002/fam.810030408.
- 481 [11] K.T. Paul, Characterization of the burning behaviour of polymeric materials, Fire Mater. 8
 482 (1984) 137–147. doi:10.1002/fam.810080304.
- 483 [12] J.M. Buist, S.J. Grayson, W.D. Woolley, eds., Fire and Cellular Polymers, Springer
 484 Netherlands, 1986. doi:10.1007/978-94-009-3443-6.
- 485 [13] M.J. Scudamore, P.J. Briggs, F.H. Prager, Cone calorimetry a review of tests carried out
 486 on plastics for the association of plastic manufacturers in Europe, Fire Mater. 15 (1991) 65–
 487 84. doi:10.1002/fam.810150205.
- 488 [14] J.G.Q. Thomas G. Cleary, Flammability characterization of foam plastics (NISTIR 4664),
 489 1991.
- 490 [15] M. Modesti, A. Lorenzetti, F. Simioni, M. Checchin, Influence of different flame retardants
 491 on fire behaviour of modified PIR/PUR polymers, Polym. Degrad. Stab. 74 (2001) 475–479.
 492 doi:10.1016/S0141-3910(01)00171-9.
- 493 [16] A. Tewarson, R.F. Pion, Flammability of plastics-I. burning intensity, Combust. Flame. 26
 494 (1976) 85–103. doi:10.1016/0010-2180(76)90059-6.
- 495 [17] M. Modesti, A. Lorenzetti, Improvement on fire behaviour of water blown PIR-PUR foams:
 496 use of an halogen-free flame retardant, Eur. Polym. J. 39 (2003) 263–268. doi:10.1016/S0014497 3057(02)00198-2.
- 498 [18] A.P. Mouritz, A.G. Gibson, Fire properties of polymer composite materials, Springer, 2006.
 499 doi:10.1007/978-1-4020-5356-6.
- 500 [19] M.L. Auad, L. Zhao, H. Shen, S.R. Nutt, U. Sorathia, Flammability properties and
 501 mechanical performance of epoxy modified phenolic foams, J. Appl. Polym. Sci. 104 (2007)
 502 1399–1407. doi:10.1002/app.24405.
- J.P. Hidalgo, J.L. Torero, S. Welch, Fire performance of plasterboard-insulation assemblies
 consisting of closed-cell charring insulation materials, in: Conf. Proc. Fourteenth Int.
 Interflam Conf., 2016: pp. 1507–1518.
- 506 [21] D.D. Drysdale, Fundamentals of the fire behaviour of cellular polymers, in: J.M. Buist, S.J.
 507 Grayson, W.D. Woolley (Eds.), Fire Cell. Polym., Springer Netherlands, Dordrecht, 1986:
 508 pp. 61–75. doi:10.1007/978-94-009-3443-6_4.
- 509 [22] B. Meacham, B. Poole, J. Echeverria, R. Cheng, Fire safety challenges of green buildings,
 510 Springer, 2012. doi:10.1007/978-1-4614-8142-3.
- 511 [23] U. Krause, W. Grosshandler, L. Gritzo, The International FORUM of fire research directors:
 512 a position paper on sustainability and fire safety, Fire Saf. J. 49 (2012) 79–81.
 513 doi:10.1016/j.firesaf.2012.01.003.

- 514 [24] BS EN 13501-1:2007+A1:2009 Fire classification of construction products and building 515 elements. Classification using test data from reaction to fire tests, 2007.
- 516 [25] BS EN 1363-1:2012 Fire resistance tests. General requirements, 2012.
- 517 [26] J.P. Hidalgo, S. Welch, J.L. Torero, Performance criteria for the fire safe use of thermal
 518 insulation in buildings, Constr. Build. Mater. 100 (2015) 285–297.
 519 doi:10.1016/j.conbuildmat.2015.10.014.
- J.P. Hidalgo, S. Welch, J.L. Torero, Design tool for the definition of thermal barriers for
 combustible insulation materials, in: Proc. 2nd IAFSS Eur. Symp. Fire Saf. Sci., 2015: pp.
 166–170.
- 523 [28] D. Drysdale, An Introduction to Fire Dynamics, 3rd ed., Wiley, 2011.
- 524 [29] B. Moghtaderi, V. Novozhilov, D. Fletcher, J.H. Kent, An integral model for the pyrolysis
 525 of non-charring materials, Fire Mater. 21 (1997) 7–16.
- 526 [30] J.E.J. Staggs, Simple model of polymer pyrolysis including transport of volatiles, Fire Saf.
 527 J. 34 (2000) 69–80. doi:10.1016/S0379-7112(99)00043-0.
- [31] C. Lautenberger, C. Fernandez-Pello, Generalized pyrolysis model for combustible solids,
 Fire Saf. J. 44 (2009) 819–839. doi:10.1016/j.firesaf.2009.03.011.
- 530 [32] S.R. Wasan, P. Rauwoens, J. Vierendeels, B. Merci, An enthalpy-based pyrolysis model for
 531 charring and non-charring materials in case of fire, Combust. Flame. 157 (2010) 715–734.
 532 doi:10.1016/j.combustflame.2009.12.007.
- [33] N. Bal, G. Rein, On the effect of inverse modelling and compensation effects in
 computational pyrolysis for fire scenarios, Fire Saf. J. 72 (2015) 68–76.
 doi:10.1016/j.firesaf.2015.02.012.
- [34] BS 476-15:1993, ISO 5660-1:1993 Fire tests on building materials and structures. Method for
 measuring the rate of heat release of products, 1993.
- J.P. Hidalgo, J.L. Torero, S. Welch, Experimental characterisation of the fire behaviour of
 thermal insulation materials for a performance-based design methodology, Fire Technol.
 (in press). doi:10.1007/s10694-016-0625-z.
- [36] R. Carvel, T. Steinhaus, G. Rein, J.L. Torero, Determination of the flammability properties
 of polymeric materials: a novel method, Polym. Degrad. Stab. 96 (2011) 314–319.
 doi:10.1016/j.polymdegradstab.2010.08.010.
- J. V Beck, Thermocouple temperature disturbances in low conductivity materials, J. Heat
 Transfer. 84 (1962) 124–131. doi:10.1115/1.3684310.
- 546 [38] P. Reszka, In-depth temperature profiles in pyrolyzing wood, University of Edinburgh,547 2008.
- 548[39]B. Schartel, T.R. Hull, Development of fire-retarded materials—interpretation of cone549calorimeter data, Fire Mater. 31 (2007) 327–354. doi:10.1002/fam.949.
- 550 [40] J.P. Hidalgo, P. Pironi, R.M. Hadden, S. Welch, A framework for evaluating the thermal

- behaviour of carbon fibre composite materials, in: Proc. 2nd IAFSS Eur. Symp. Fire Saf.
 Sci., 2015: pp. 195–200.
- 553 [41] C. Di Blasi, Modeling and simulation of combustion processes of charring and non-554 charring solid fuels, Prog. Energy Combust. Sci. 19 (1993) 71–104. doi:10.1016/0360-555 1285(93)90022-7.
- 556 G. Rein, C. Lautenberger, A.C. Fernandez-Pello, J.L. Torero, D.L. Urban, Application of [42] 557 genetic algorithms and thermogravimetry to determine the kinetics of polyurethane foam smoldering combustion, Combust. Flame. (2006)95-108. 558 in 146 559 doi:10.1016/j.combustflame.2006.04.013.
- 560 [43] C.L. Beyler, M.M. Hirschler, Thermal decomposition of polymers, in: SFPE Handb. Fire
 561 Prot. Eng. 2, 1995: pp. 111–131.
- 562 [44] A.A. Stec, T.R. Hull, Assessment of the fire toxicity of building insulation materials, Energy
 563 Build. 43 (2011) 498–506. doi:10.1016/j.enbuild.2010.10.015.
- 564 [45] V. Mozer, M. Smolka, P. Tofilo, Threat level assessment of smoke emissions from 565 compartment boundaries, in: 2nd Eur. Symp. Fire Saf. Sci., 2015: pp. 284–288.