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Multi-scale Experiments of Household Materials Burning

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In France, one home fire occurs every 2 minutes and these accidents account for 10,000 victims each year. Majority of home fires can spread very quickly because of polymer materials, increasingly used in dwelling houses. Currently, modeling fire development to aid the scale-up from bench to full scale is a big challenge. Studies combining experiments and modeling at increasing scale have already been performed. In this work, radiant panel with heat flux concentrator has been developed and used to study the combustion of household materials. The area of radiative source is equal to 2 m². Ignitability, mass loss and smoke composition (CO, CO_2 and O_2) data have been recorded to evaluate heat release rate. The results have been compared with those from cone calorimeter on small samples (100 cm²) at 50 kW/m² in order to study the scale effect of the testing device.

1. Introduction

In France, one home fire occurs every 2 minutes and these accidents account for 10,000 victims each year. Majority of home fires can spread very quickly because of polymer materials, increasingly used in dwelling houses (European Flame Retardants Association (EFRA), 2011). Indeed, for 40 years, materials (such as wood, metals) traditionally used in construction, transport or houses were gradually replaced by polymers (more commonly known as "plastics") or polymer composites. Composition of these polymeric materials is conducive to the start of a fire, which is often rapid and violent. They also generate highly toxic fumes. Efforts have been made to evaluate the gravity of fire and organize firemen intervention, Alexandridis et al. (2011) predicts the velocity at which a fire will spread and estimates the released heat of the fire. However, the large scale transfer of small fire tests emerges as the major problem encountered by researchers. Therefore, it is difficult to predict and anticipate the development of a full-scale fire. To solve this problem, the development of an approach combining experiments and modeling is necessary. Moreover, multi-scale analysis is the required strategy. Bustamante Valencia (2009) and Marquis (2010) identify four levels of scales in the literature:

- Micro scale (with thermo gravimetric analysis, pyrolysis combustion flow calorimetry and pyrolysis-GC/MS)
- Small scale or Material scale (with cone calorimeter)
- Product scale (with radiant panel and medium burning item test)
- Macroscopic scale (with room corner test)

According to Bal and Rein (2011), the best material for investigating the ignition of a solid is polymethyl methacrylate (PMMA). PMMA is a material for which many experimental data, numerical studies and properties are listed in the literature. The decomposition mechanism of PMMA (i.e. depolymerization) is also

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well known. The combustion of PMMA is composed of three steps: (a) When PMMA is subjected to an external source of heat, it decomposes to 99% by releasing the methyl methacrylate monomer (MMA). Wampler (2006) verifies this affirmation by Pyrolysis GC/MS. (b) Then, the decomposition of MMA produces small fuel molecules such as methanol, methane, formaldehyde, propylene, 2-methyl propylene and acetone. (c) Finally, these molecules will react with oxygen in the air to produce carbon dioxide (CO_2), carbon monoxide (CO) and water (H_2O) (Zeng et al., 2002a) (Zeng et al., 2002b).

Many studies are performed at laboratory scale to characterize the ability of a material to ignite and propagate fire. But the behavior of a polymer at real scale may significantly differ from observation made at small scale. This paper deals with a comparison of experimental tests performed with household materials at different scales (i.e. different devices). Tests are initially performed with the cone calorimeter where samples of 100 cm^2 are exposed to a 50 kW/m^2 heat flux. Characteristic information of the material is obtained from the measurements of the ignitability, mass loss and smoke composition (CO, CO_2 and O_2) data have been recorded to evaluate heat release rate (HRR). To characterize the scale transfer, secondary tests are performed with the radiant panel. This experimental device is developed at Ecole des Mines d'Alès. This device is associated with a concentrative device in order to provide sufficiently high heat fluxes on the test samples. Size of square samples is 100 cm^2 and the received heat flux is 50 kW/m^2. The characteristic information of the material is the same as that obtained in the cone calorimeter test. These key properties may be used in a fire modelling (Tavelli et al., 2013) as parameters to predict mass loss (ML) of material and the rate at which heat is generated by fire (HRR) for full-scale fire scenario.

2. Materials and methods

2.1 Material

Material used in this study is a clear neat PMMA (AbaquePlast, France) and synthesized via anionic polymerization. The parameters experimental values are listed in Table 1. The sample dimensions were 10 cm long, 10 cm wide and 4 mm thick with a mass of 45.2 ± 2.9 g.

Table 1: Set of the parameters experimental and numerical values for clear PMMA

Parameters	Experimental values	Numerical values	References
Density, ρ (kg/m^3)	1190	[1170-1200]	(Mark, 2006) (Trotignon et al., 1994) (Vovelle and Delfau, 1997) (Lyon and Janssens, 2005)
Thermal conductivity, k (W/m.K)	0.20	[0.167-0.251]	
Specific heat, c (J/kg.K)	1400	[1400-1520]	
Surface emissivity, ε (-)	0.86		
Thermal diffusivity, α (m^2/s)	1.2×10^{-7}	[1.1×10^{-7}-1.4×10^{-7}]	
Pre-exponential factor, A (1/s) in N_2	2.9×10^{13}	6.5×10^{13}	(de Wilde, 1987)
Activation energy, E (kJ/mol) in N_2	221	233	

2.2 Methods

<u>Cone calorimeter</u>

The PMMA reaction-to-fire characterization was carried out in a cone calorimeter Standard ISO 5 660 (AFNOR, 2002) made by Fire Testing Technology (FTT) (Babraukas, 1984). **Errore. L'origine riferimento non è stata trovata.** shows a schematic view of the cone calorimeter with a solid PMMA matrix in the sample holder exposed to irradiance through an electric heater.

Several heat flux levels can be used: from 10 to 75 kW/m^2. Tests were carried out with a piloted ignition. The ignition spark is positioned above the sample up to ignition. In this study, the fire behavior produced by samples placed in horizontal or vertical position is investigated. This apparatus can provide information on materials relevant to their fire performance for example critical heat flux for ignition, ignition time, HRR, productions of smoke and toxic gases… The HRR is determined using the oxygen consumption technique. That is based on the fact that the majority of plastics, rubbers and natural organic materials produce 13.1 MJ/kg of oxygen consumed with an accuracy of ± 5% (Huggett, 1980). The sample dimensions were 10 cm long, 10 cm wide and 4 mm thick (i.e. 88.4 cm^2 exposed surface). For the horizontal and vertical orientation, the standard preparation technique requires that the sides and base of the specimen are covered by aluminum foil of a specified thickness. All specimens are positioned in a sample-holder containing a refractory fiber insulating in the back side. In this study, the vertical orientation is important in order to directly compare the results obtained from the small scale to the product scale.

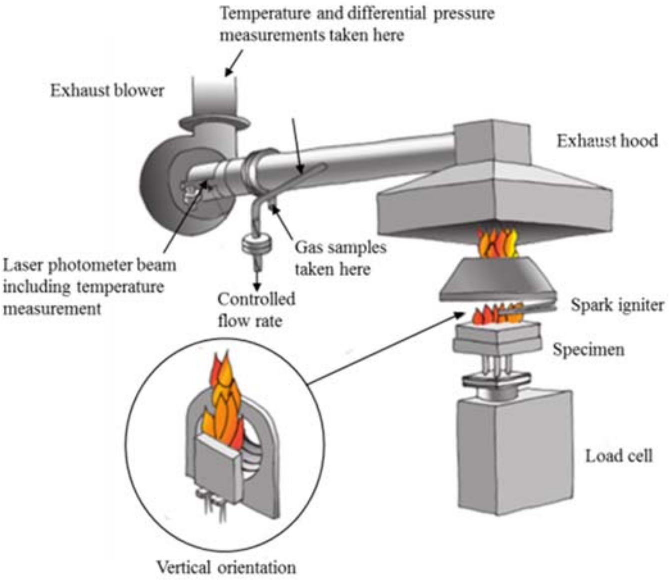

Figure 1: Schematic layout of cone calorimeter

Radiant panel (RP) and its concentrator

Figure 2 is a schematic representation of this experimental device. It is developed at Ecole des Mines d'Alès and it is a 1 m x 2 m wall made up with 2 radiant panels depending on the test configuration (Figure 3). Maximum electrical power of the radiant panel is 120 kW. In the present study, the radiative surface consists of two 60 kW panels because this setup allows producing an emitted heat flux of 118 kW/m². The panels are equipped with 3 kW short-wave infrared halogen lamps with a temperature color of 2400 K and a maximum radiation at a wavelength of about 1.2 microns.

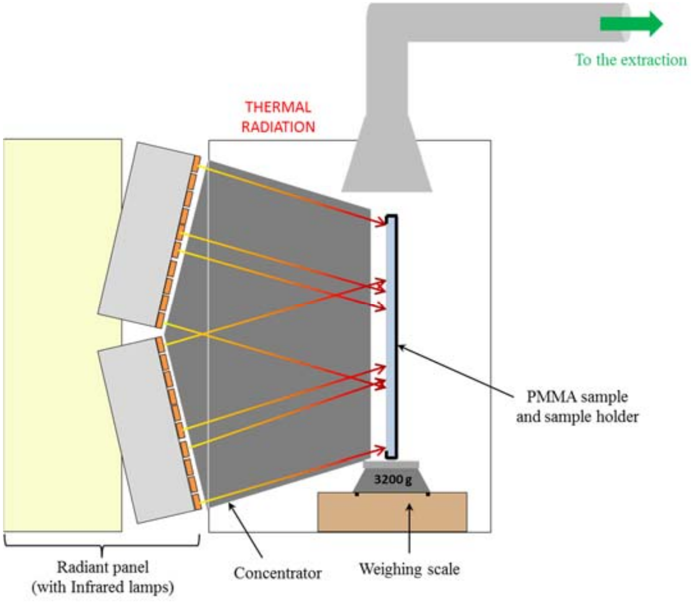

Figure 2: Schematic representation of new fire process; the radiant panel and its concentrator (side view)

Figure 3: RP configuration – 2 x 60 kW

It noticed the lamps spectrum varies from 0.5 microns (visible) to 4.5 microns (far IR). The inclinations of panels can be modified to concentrate radiative heat flux on test sample. A preliminary study was performed to determine the optimal configuration with an ideal inclination of 13° corresponding to a gain of 20 % on the flux received by the target. Figure 4 presents the variation of received heat flux on/by the target according to the distance from RP at the maximum emitted heat flux (118 kW/m²). Figure 4 clearly shows the efficiency of the concentrator which maintains a constant heat flux of 78 kW/m² until one meter from RP. On the contrary, when the RP is used without concentrator, the radiative heat flux received by target decreases with the distance from RP.

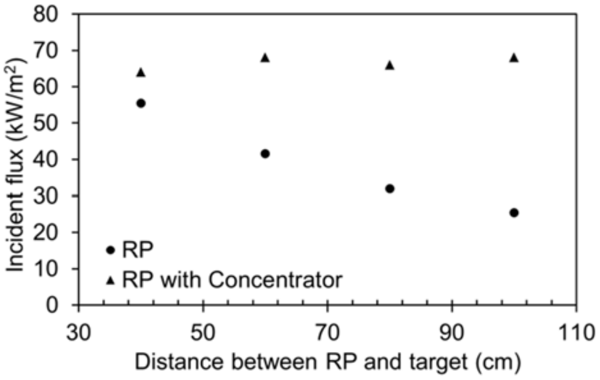

Figure 4: Effect of the concentrator on the flux received by the target

The sample is located in a sample holder containing a refractory fiber insulating backside and is placed in vertical orientation. The addition of the concentrator to the radiant panel provides a new device: RAPACES (RAdiant PAnel Concentrator Experimental Setup).

2.3 Measurements

All the tests are performed with tests samples in vertical position exposed to a radiative heat flux of 50kW/m². The characterization can be performed in two modes: visual inspection and a more quantitative characterization. The visual inspection is a qualitative characterization: it is observed through the evaluation of thermal degradation (formation of gas bubbles, release of fuel vapors, flame height ...).Techniques used to quantify material degradation are:

- A CAPTEC flux meter with a sensibility equal to 13.1 µV/(W/m^2). The sensor size is 5 cm x 5 cm. This utility is to determine the received flux by the target.
- A SERVOMEX Series 4100 gas analyzer enables to quantify CO, CO_2 and O_2 concentrations during the combustion of the material.
- A KERN weighing scale enables to measure the mass loss of material in function of time with a uncertainty of 0.5 g on the measurements.

3. Results and discussions

The aim of this study is the comparison of data (i.e., time ignition, mass loss and heat release rate) obtained in cone calorimeter and in RAPACES.

3.1 Ignition time

To determine the level of flammability hazard based on ignitability, the first information needed is the ignition time. Tests are performed with piloted ignition. Table 2 highlights the effect of different sample surface preparations on time to ignition in cone calorimeter (CC) and RAPACES. As regards the polymer surface properties, fire tests have been performed either on transparent samples or on samples covered by a thin layer of graphite. As highlighted in Table 2, adding a layer of graphite on the sample has only a small influence on ignition time when tests are carried out with cone calorimeter (decrease of only 4 seconds). On the opposite, adding graphite makes the ignition time about 30 seconds lower when fire tests are carried out with RAPACES.

Table 2: Comparison of ignition time between CC and RAPACES at 50 kW/m²

Device	Ignition time (s)	
	Without graphite	With graphite
CC	29 ± 2	25 ± 2
RAPACES	55 ± 2	23 ± 2

The explanation to this discrepancy can be found in Table 3 and Table 4. Wavelength ranges of emission spectra of the two devices are different. RAPACES emits essentially in the near infrared range while cone calorimeter emits in the middle infrared range. The absorption spectrum of the non-recovered polymer indicates that PMMA is transparent and begins to absorb radiations from 2 µm (i.e. 0 % transmission) (Boulet et al., 2014) whereas PMMA covered with graphite absorbs radiations on the whole range of wavelengths.

Table 3: Emission spectrums between CC and RAPACES

Device	Wavelengths range (µm)
CC	1.8 - 11
RAPACES	0.5 – 4.5

Table 4: Absorption spectrums of transparent PMMA and PMMA with graphite

Material	Wavelengths range (µm)
Transparent PMMA	2.0 - 25
PMMA with graphite	0 – 25

3.2 Mass loss (ML) and Heat Release Rate (HRR) for graphite covered samples

Once the sample is ignited, the mass loss curve can be drawn. As represented in the Figure 5, there is a marked difference between the curves obtained with the two devices. In fact, the derivate of the ML curve (Mass Loss Rate) for RAPACES is way higher than the one for CC. In terms of kinetics of combustion, this means that a sample of PMMA, receiving the same incident flux, burns faster when using RAPACES.

To understand the fire behavior of a material, the determination of the heat release rate is essential. (Babraukas, 1984) indicates that the HRR is the most significant parameter for the fire hazard material evaluation, since it controls the rate of growth in fire, including heat and ultimately the amount of smoke and toxic gas generated. Several methods for estimating the HRR exist. Some are based on experimental tests while others are trying to describe the phenomena by solving complex equations. Two ways to measure the energy released are presented:

- Measure the quantity of oxygen consumed: the amount of energy produced is derived by multiplying the mass of oxygen consumed in kilograms per 13 000 kJ. Energy flow is given by the Eq(1):

$$HRR\ (t) = E \times \left(\frac{D}{e}\right) \times \left(X_{O2}^{0} - X_{O2}\right) \tag{1}$$

Where E is the Thornton factor (equal to 17.35 MJ/m^3), D is the suction flow (m^3/s), e is the air expansion factor (equal to 1.105), X_{O2}^{0} is the oxygen volumetric fraction in the standard conditions (equal to 0.2095) and X_{O2} is the oxygen volumetric fraction at time t.

- Measure the mass loss rate of fuel: energy flow obtained according to the Eq(2):

$$HRR\ (t) = \chi \times MLR(t) \times \Delta H_c \tag{2}$$

Where χ the efficiency of the combustion reaction, MLR is the mass loss rate (g/s) and ΔH_c is the heat of combustion (kJ/g). The first method is chosen in order to properly compare the two devices. Figure 6 confirms that the kinetics of combustion for RAPACES is faster. The burning time with RAPACES is twice shorter than an experiment with CC. It can also be seen that in this case the HRR peak is higher (1340 kW/m² vs 947 kW/m²). It is assumed that those differences may be attributed to difference in flux absorption by the material. Indeed, as previously mentioned, CC and RAPACES exhibit different emission spectra. Despite the presence of the graphite layer, it is suspected the absorbed heat flux could vary with time and surrounding atmosphere temperature. However, more experiments are necessary to better understand this behavior.

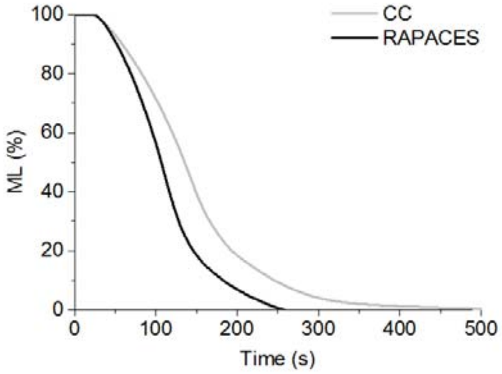

Figure 5: Mass loss as a function of experimental time

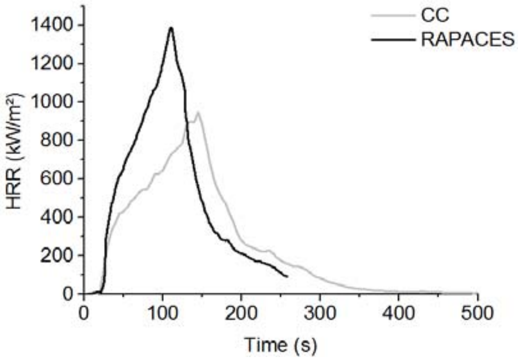

Figure 6: Heat release rate as a function of experimental time

Finally, the total heat releases (THR) are compared. THR is equal to the area under the curve representing the HRR relative to the pyrolysis temperature. The similar values of THR (24.5 kJ/g) show that PMMA releases the same total heat in both devices close to the theoretical heat of combustion (25 kJ/g) indicating that the combustion efficiency is similar with both apparatus and close to 1.

4. Conclusions

Two devices have been used in order to investigate the behavior of PMMA samples exposed to a radiative flux. The two devices are the cone calorimeter and the new apparatus called RAPACES.

Several parameters have been analyzed in order to compare the two devices: ignition time, mass loss, heat release rate and total heat release. The experiments have all been performed keeping the same heat flux (50 kW/m²) and employing only 10 cm x 10 cm sized samples. Samples have been placed with vertical orientation and the effect of a layer of graphite over the surface has been tested.

Ignition time is influenced by the different emission spectra between CC and RAPACES when PMMA is clear. The experimental results show how the thermal degradation behaves differently between the two devices. In fact, with RAPACES, kinetics of combustion is faster bringing to a higher peak of HRR.

In order to better characterize RAPACES and go further in the study adding the influence of higher sample's sizes and fluxes.

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