



Experimental determination of the evolution of the incident heat flux received by a combustible during a cone calorimeter test - influence of the flame

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Abstract:

The degradation kinetic of polymeric materials in a cone calorimeter strongly depends on the irradiance level imposed at the sample's surface. Indeed, even if the irradiance level is supposed to be kept constant during cone calorimeter test, the amount of heat flux which is emitted by the exothermic combustion reactions (flaming process) can greatly increase the total heat flux received by the material. Analytical treatment on recently obtained results of an acrylonitrile-butadiene-styrene's mass loss rate with controlled atmosphere cone calorimeter have shown that the differences observed between well ventilated and inert environment can be attributed to the impact of the flame. This observation has brought the necessity to determine the impact of the flaming process on the material thermal decomposition. To do so, a series of experiments has been devised, based on the insertion of a heat fluxmeter within the matrix of an acrylonitrile butadiene styrene material, during cone calorimeter tests to measure the flame heat flux as a function of the decomposition and the combustion processes.

Keywords: flux measurements, radiation, thermal degradation, controlled atmosphere cone calorimeter

1. Introduction and context

From a research point of view, incident heat flux received at the surface of a material when using a cone calorimeter is an important matter, since it has been shown that, it can have a large influence on the thermal degradation process, the combustion, and the gaseous emissions [1], [2], [3]. Moreover, the results obtained are usually used as the basis of numerical models and subsequently integrated as a part of Computational Fluid Dynamics (CFD) modelling. In order to use these models with predictive objectives, several input parameters must be determined. To ensure that the calculation cannot be skewed, the data used must be as accurate as possible. Input data used in codes is extensive, however the most important aspect in focusing on the thermal degradation of a material, is the heat flux really received at the surface of this material when exposed to real fire or to any standardized fire test method.

Nowadays, the experimental apparatus frequently used for reaction to fire tests is the cone calorimeter described into the ISO 5660 standard [4]. The principle of this apparatus is to expose a piece of material to a constant heat flux, calibrated before testing, which allows simulating a flame impacting the material's surface. Different irradiance levels can be tested to assess the reaction to fire of the material, evaluated using key parameters such as mass loss, Mass Loss Rate (MLR) or its Heat Release Rate (HRR). In this context, the ability to control the test parameters and especially the heat flux value received at the material's surface is primordial. Cone calorimeter design doesn't allow varying the radiative flux at the surface of a material. Thus the emitted heat flux from the heater is kept constant during the test and it is assumed to be constant also when processing the results. However, the heat flux at surface boundary can vary greatly throughout the test, especially when a flame appears at the surface of the material: the radiative feed-back from the flame to the surface of the material is then added to the incident irradiance from the cone calorimeter heater [5], [6].

As a part of an overall project on the determination of the reaction to fire of polymeric material in enclosed environments, Controlled Atmosphere Cone Calorimeter (CACC) tests have been performed to determine notably the possible occurring ignition conditions of an Acrylonitrile Butadiene Styrene (ABS) [7]. Results of these tests have shown:

- Firstly, as expected that the combustion is no longer possible below a certain oxygen level.
- Secondly, that the degradation kinetic of ABS is strongly related to the presence of the flame. Indeed, simple calculations presented in the next section have shown that the proportion of the MLR due to flame impact can be found back comparing MLR curves in well ventilated and inert environments. Thereby, the necessity of determining the flame heat flux for the ABS material (as for others) has emerged.

Several models have been constructed to determine the MLR of materials in evaluating the variables that can enhance or reduce this parameter. Tewarson [8] proposes a model taking into account notably the net heat flux received at the material's surface as follows:

$$\dot{m}'' = \frac{(\dot{q}_e'' + \dot{q}_{fr}'' + \dot{q}_{fc}'' - \dot{q}_{rr}'')}{\Delta H_g} \quad (1)$$

Where:

- \dot{m}'' : Mass loss rate (g.m⁻².s)
- \dot{q}_e'' : External heat flux applied to the surface (kW.m⁻²)
- \dot{q}_{fr}'' : Flame radiative heat flux transferred to the surface (kW.m⁻²)
- \dot{q}_{fc}'' : Flame convective heat flux transferred to the surface (kW.m⁻²)
- \dot{q}_{rr}'' : Reradiation loss (kW.m⁻²)
- ΔH_g : Heat of gasification (kJ.g⁻¹)

Tewarson has thus shown that the net heat flux is the addition of all component fluxes at the surface of the exposed to fire material. As the flame provides an important amount of energy once established, it is necessary to characterize the heat flux values that can be reached at the surface of the material. Indeed, a better knowledge on the flame heat flux is essential to develop methodologies that can predict the development of fires. The objective of the present work is thus to determine the variation of heat flux received at the surface of an ABS sample material, during cone calorimeter tests.

Several studies have focused on the determination of the flame heat flux for a range of solid fuels and in different apparatuses. A non-exhaustive review of the available data has been summarized in the table below.

Table 1: Main references on flame heat flux measurements available in literature

Date	Authors	Apparatus	Measurement technic	Material	Tested conditions	Mean flame heat flux (kW.m ⁻²)	
1981	Tewarson <i>et al.</i> [9]	Advanced Flammability Measurements apparatus (AFM) Two apparatuses used to test different material exposed surface (0.0068 and 0.073 m ²)	Determined numerically from experimental measurements (MLR and gaseous species concentration)	POM (0.0068m ²)	Irradiance level increasing and variation of the oxygen concentration (chosen here to be closest to well ventilated conditions) Results given for steady state flame heat flux	23.3%O ₂ (wt)	Rad 2 Conv 25 Tot 27
				POM (0.073m ²)		23.3%O ₂ (wt)	Rad 9 Conv 21 Tot 30
				PMMA (0.0068m ²)		20.7%O ₂ (wt)	Rad 7 Conv 17 Tot 24
				PMMA (0.073m ²)		23.3%O ₂ (wt)	Rad 17 Conv 13 Tot 30
				PP (0.0068m ²)		20.8%O ₂ (wt)	Rad 14 Conv 15 Tot 29
				PP (0.073m ²)		23.3%O ₂ (wt)	Rad 23 Conv 12 Tot 35
				PS (0.0068m ²)		23.3%O ₂ (wt)	Rad 27 Conv 11 Tot 38

Date	Authors	Apparatus	Measurement technic	Material	Tested conditions	Mean flame heat flux (kW.m ⁻²)	
						1 st method	2 nd method
1981	Santo &Tamanini [10]	Advanced Flammability Measurements apparatus (AFM)	Determined numerically from experimental measurements (Flame temperature and emittance, MLR, flame shape and radiative power per unit height) Two methods have been used for calculation (see details in [10])	PMMA	Irradiance level increasing and variation of the oxygen concentration Results given for steady state flame heat flux	27.9	30.2
						28.9	29.2
1994	Rhodes [6]	Cone calorimeter	Heat flux meter inserted in the matrix (1 inch and 1/8 inch)	PMMA	Irradiance level increasing up to 200kW.m ⁻² Results given for steady state flame heat flux	15 kW.m ⁻²	18
						19 kW.m ⁻²	29.5 ± 1
						24 kW.m ⁻²	36
						25 kW.m ⁻²	22± 2.4
						33 kW.m ⁻²	20
						37 kW.m ⁻²	23
						41 kW.m ⁻²	40
						50 kW.m ⁻²	21.5 ± 1.9
						52 kW.m ⁻²	43
						62 kW.m ⁻²	30
63 kW.m ⁻²	10						
75 kW.m ⁻²	14.25 ± 4.9						
2005 & 2008	Beaulieu [11], Beaulieu & Dempsey [12]	Advanced Flammability Measurements apparatus (AFM)	Total flame heat flux : ¹ Heat flux meter inserted in the matrix ² Micro-foil heat flux sensor Convective and radiative heat flux : ¹ Radiative heatflux meter (difference between individual sensors for radiative and total measurement) ² Difference between total heatflux meter data collected at the surface and 0.64cm recessed below the surface.	PMMA PP POM	Irradiance level increasing up to 200kW.m ⁻² Results given for steady state flame heat flux	Rad	12 ± 3
						Conv	8± 3
						Tot	20± 3
						Rad	11 ± 3
						Conv	4 ± 3
						Tot	15 ± 3
						Rad	0 ± 3
						Conv	11 ± 3
						Tot	11 ± 3
						2015	Li <i>et al.</i> [13]

* Rad: Radiative impact; Conv: Convective impact; Tot: Total impact; POM: Polyoxymethylene ; PMMA: Polymethylmetacrylate; PP: Polypropylene; PS: Polystyrene; MDF: Medium Density Fibreboard

This short review shows that only a few experiments have been realized, to determine the evolution of the flame heat flux at the surface of solid materials. Furthermore, a number of the cited references do not include a direct flame heat flux measurement but algebraic methods, to determine this parameter from other measurements such as MLR or radiative properties of the flame. These results have however been considered because of the limited number of reference publications on flame heat flux measurement. From the results presented here, it can be seen that the flame heat flux strongly depends on the type of tested material and on the testing scale. Moreover the results highlight huge disparities between materials. Indeed, the range of flame heat fluxes values extends from 4.5kW.m⁻² for MDF to 40kW.m⁻² for PMMA with values for thermoplastic materials generally at the higher end of the range. In considering the presented values and the fact that ABS is itself a thermoplastic material, the flame heat flux results for this specific material can be expected to be between 15 and 30kW.m⁻².

The work presented in this paper concerns in the first place a review of previously obtained results on ABS material using a CACC which led to the emergence of the flame heat flux study. In this section, an experimental flame heat flux determination method based on MLR analysis will be presented. In the following sections, the experimental protocol used to determine experimentally the heat flux received at the surface of the ABS material will be presented as well as the results obtained during the series of tests. Results for three different heat fluxes (20, 35 and 50kW.m⁻²) will be analyzed and the issue concerning the non-linearity of the heat flux during cone calorimeter tests, when degradation process (pyrolysis) is associated with combustion process will be discussed.

2. Experimental flame heat flux determination

Analytical reviews of the results of ABS MLR under air and nitrogen have been led [7] and an interesting tendency has been observed. Indeed, in multiplying the MLR results obtained at 21% [v/v] oxygen concentration by a certain coefficient and dividing the time by the same coefficient, curves for 0% [v/v] can be obtained. Moreover, this happened to be true for different irradiance levels imposed at the surface material. Examples are given for two different irradiance levels in Figure 1.

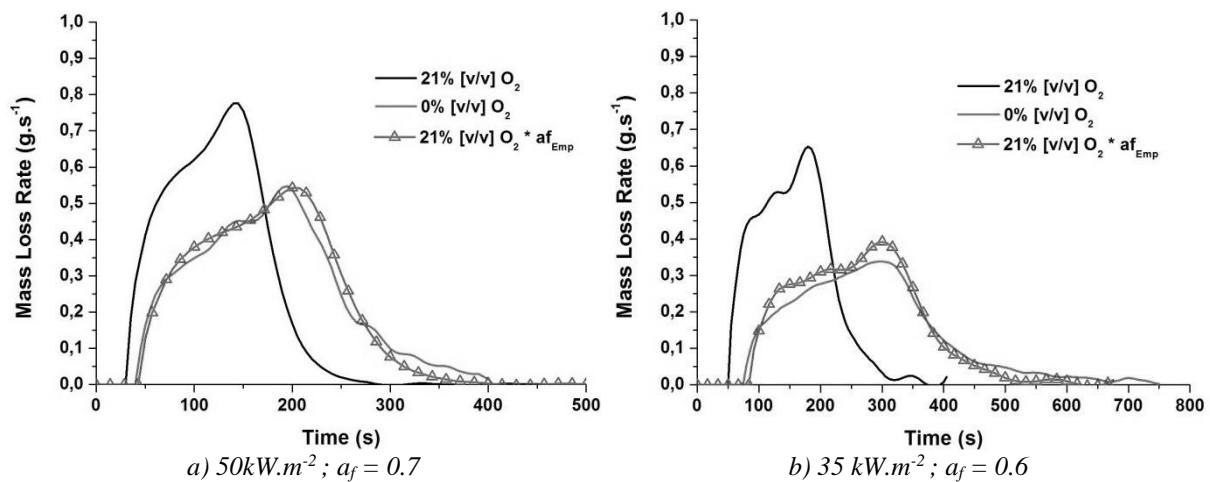


Figure 1: Mass Loss Rate curves for ABS material at 21% [v/v] and 0% [v/v] oxygen concentration volume in CACC and modified curves using 0.7 and 0.6 $a_{f_{Emp}}$ coefficient values

It should be noted that this type of calculation can be performed only in respect of the two following conditions and thus cannot be applied to any kind of material:

- The same quantity of material must be degraded during the test. It means that the material must be degraded in its entirety or at least the remaining masses after testing (quantities of residues) must be equivalent for the two considered conditions (*i.e.* MLR integrals must be identical).
- Condensed phase chemical processes should not be affected by the presence of oxygen and thus the degradation must only be driven by thermic

Concerning the ABS material, the two aforementioned conditions have been verified. For the first one, comparisons between the initial and final masses have been performed to determine if the MLR for the different conditions can be compared without introducing a bias. Results for the different experiments presented before (Figure 1) are available in the table below.

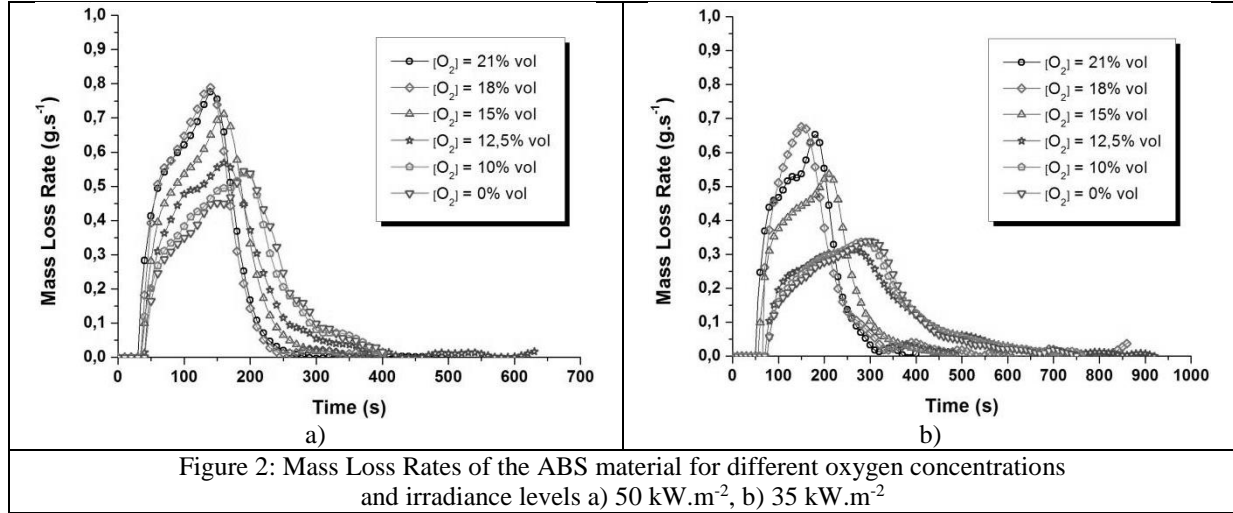
Table 2 : Initial and final masses of the tested samples

Tested condition	50kW.m ⁻² - 21% [v/v]	50kW.m ⁻² - 0% [v/v]	35kW.m ⁻² - 21% [v/v]	35kW.m ⁻² - 0% [v/v]
Initial mass	32.14	31.82	31.90	32.34
Final mass	1.32	1.47	1.24	2.03
Total mass loss	30.82	30.35	30.66	30.31

Table 2 highlights that there are only slight differences between tests in terms of mass loss. Indeed, the mean mass loss on the four presented tests is 30.54g and the standard deviation associated is 0.24g.

For the second condition, it has been proven previously [7] that the decomposition of the ABS material occurs in one single step and that the chemical process occurring in condensed phase is not oxygen dependent. Indeed, the only way the oxygen concentration affects the degradation is in allowing or not the existence of a

flaming process associated with the degradation process which thus provides a thermal feedback to the surface of the material, enhancing the MLR. Figure 2 highlights this specific degradation behaviour.



Considering differences observed in MLR kinetics on Figure 2 a) and b), it can be concluded that the MLR of the ABS material depends of both the heat flux imposed at the surface material and the oxygen concentration. Although, the oxygen concentration have an effect only in dictating the combustion regime that can be associated with the degradation process in condensed phase. Details on the combustion regimes that can be observed for ABS in a CACC in reducing the oxygen concentration can be found in [7]. Below a certain oxygen concentration, a combustion process is no more possible (below 12.5% [v/v] for the 50kW.m⁻² condition and below 15% [v/v] for 35kW.m⁻²). Since then the MLR kinetic is no longer modified in decreasing the oxygen concentration which proves that the oxygen concentration does not affects the degradation process occurring in the condensed phase.

As the conditions are respected, the aforementioned calculation can be performed with good confidence in the methodology. This type of calculation can be expressed analytically using (1). The coefficient a_{fEmp} represents the amount of MLR which can be attributed to the presence/absence of flaming process.

$$MLR = f(t, Y_{O_2})$$

$$MLR(t, Y_{O_2} = 0\%) = a_{fEmp} * MLR\left(\left(\frac{t}{a_{fEmp}}\right), Y_{O_2} = 21\%\right) \quad (2)$$

Where:

MLR : Mass Loss Rate

t : Reference time for the test

a_{fEmp} : Empirical multiplier coefficient representing the amount of MLR due to the flame impact

Unfortunately, the a_f coefficient cannot be calculated directly and has to be estimated empirically from experimental results. For the two specific presented conditions, a_{fEmp} has been determined to be 0.7 and 0.6, respectively for the 50 and 35kW.m⁻² irradiance level conditions.

These results have highlighted the need for determination of the flame heat flux, which impact seems to explain the differences observed between the degradation kinetics at 21% [v/v] and 0% [v/v] oxygen concentration.

The aim of the experimental campaign led was thus to determine, for the ABS material, the part of the heat flux which can be attributed to the combustion phenomenon (*i.e.* the radiance potency of the flame), when the pyrolysis gaseous compounds emitted during the degradation of the polymeric are ignited. The results are presented in the next sections.

Previous works have shown that the radiative feedback when the flame is established can be determined by different techniques [6], [11], [14]. The one chosen during this work is an intrusive one, developed by Rhodes

[6] consisting in the insertion of a heat fluxmeter within the matrix of the polymeric material. Details on the specificities of the assembly required to measure flame heat flux and on the sample preparation are given in the next sections.

3. Experimental protocol

Experiments have been performed using an ISO 5660-1 [4] cone calorimeter partially unequipped. Because of the specificities of the experimental sample holder described hereafter, certain parts of the cone calorimeter apparatus have been removed: spark igniter, gaseous analysis line and weighting device. As the main objective was to measure the heat flux at the surface of the material, none of the data typically collected using cone calorimeter (mass loss, MLR, gaseous emissions) has been measured, except time to ignition.

3.1 Details on sample preparation, material and experiments performed

Material used for the study was a commercial non flame retarded ABS polymer, the chemical composition of which is unknown. Details on the material characteristics are given hereafter:

- Producer: POLYPENCO
- Commercial designation: 42400104/3MM - PLASTIQUE ABS PLAQUE
- Colour: White
- Density: 1.06
- Nominal Thickness: (3.00 ± 0.03) mm

Cone calorimeter samples nominal size has been set to $(100 \pm 0.3 * 100 \pm 0.3)$ mm to ensure conformity with ISO 5660-1 standard [4]. Their average mass has been measured to be (31.15 ± 0.07) g. Aluminium foil and silica wool have been used to ensure the backing condition as described in ISO 5660-1 standard [4]. (15 ± 1) mm diameter holes have been pierced in the centre of each sample to allow the positioning of the fluxmeter. The diminution of the exposed sample area due the pierced hole in the centreline has been calculated to be 2.2%, which is considered not to be significant enough to affect the degradation process. Samples have been conditioned before testing at (23 ± 2) °C and (50 ± 5) % RH for more than 88 hours in accordance with ISO 291 [16].

The fluxmeter which has been used to conduct the experiments is a ½ inch water cooled Schmidt-Bolter total heat flux sensor. Technical specificities, like for example 180° view angle, have been chosen in accordance with [15]. Its measure range has been calibrated from 15 to 100kW.m⁻² and the sensibility has been determined to be less than 0.15mV.kW⁻¹.m⁻². Because of the numerous uncertainties using the different technics allowing collecting the radiative part of flame only, the choice was made to measure the total heat flux emitted by the flame (*i.e.* radiative and convective part). Cooling of the sensor has been ensured for the duration of the test with room temperature water, avoiding variation of flow rate and temperature. Signal was collected continuously using an acquisition unit, and then post-processed using the appropriate conversion equation obtained during the calibration.

Ignition of the samples was piloted thanks to a 2cm flame provided by a removable methane burner positioned (13 ± 2) mm above the surface and at the centre of the sample as prescribed in ISO 5660 [4]. To avoid masking effect of the impact of flame radiation on the fluxmeter, pilot flame was removed, for each test, as soon as the ignition occurred.

Three different incident heat fluxes from the cone heater, 50, 35 and 20kW.m⁻², have been studied in order to determine if differences in the results can appear function of the irradiance levels imposed at the surface of the ABS material. For each tested condition, experiments were conducted at least three times, to ensure the accuracy of the results in considering repeatability conditions.

2.2 Sample holder

As the main objective was to measure the heat flux received at the surface of the material, one of the main challenges has been to develop a sample holder which can ensure that no differences in height can appear between the surfaces of sample and heat fluxmeter. Thus, a specific sample holder has been developed allowing the insertion of the fluxmeter at the centre of the sample and maintaining it all along the test.

The basis of the sample holder is a $(20 \pm 2 * 20 \pm 2)$ cm calcium silicate plate, with a (10 ± 1) mm thickness which supports the entire dispositive. This plate has been pierced at the centre with a (10 ± 1) mm diameter hole and cut along the x axis in two parts. A second layer of $(10 \pm 1 * 10 \pm 1)$ cm calcium silicate with

a (10 ± 1) mm thickness has been positioned at the centre of the first plate, pierced as well with the same diameter and cut along the y axis. The two plates can be assembled and disassembled, one above the other, thanks to a mortise and tenon system. The fluxmeter is laid on the second plate just above the hole. The cut along the plates and the holes at their centres allows positioning cooling pipes and wires at the fluxmeter's rear; the tenon mortise system, meanwhile, ensures the stability of both the sample holder and the fluxmeter during the experiment.

The upper layers were constituted of the tested ABS sample placed on an aluminium foil itself placed on a silica wool layer. These three layers and the second calcium silicate plate have been 'covered' by the classical cone calorimeter sample holder's upper part which allowed maintaining the whole system during the tests. To reach the exact height of the sample holder upper part, the thickness of the silica wool layer was adjusted depending on the material thickness. In this case, as the material was (3.00 ± 0.03) mm thick and the silica plate layer was (10 ± 1) mm, the silica wool layer thickness have thus been fixed to (13 ± 1) mm. As well as the sample, the aluminium foil and the silica wool layer were pieced in their centre with a (15 ± 1) mm diameter hole to receive a (15 ± 0.5) mm long stainless steel ring. This ring has been designed to insulate the heat fluxmeter from its surroundings. It allows maintaining all the components of the assembly and prevents the different layers (*i.e.* silica wool, aluminium foil and tested sample) from interacting with the fluxmeter's body in order not to skew the measurement. Indeed, the structure of the different components, especially the one of the tested sample, can evolve along the test as the degradation occurs. The stainless steel ring therefore ensured that if the material melts, it won't directly reach the body of the fluxmeter and thus affect the measurement.

The radiation from the stainless steel ring on the fluxmeter body is expected to be negligible (1) because of the cooling ensured throughout the test (2) on the direct measurement effected with the sensor element which even with a 180° vision angle cannot 'see' the stainless steel ring. Indeed the stainless ring upper position is not expected to affect the measurement as long as its top surface is not higher the surface of the sensor element of the fluxmeter.

Figure 3 below summarizes the information detailed above about the complete and complex protocol used to perform the experiments. Furthermore, Figure 4 presents two pictures which provide an overview of the mounting in its entirety and the way the different elements are assembled.

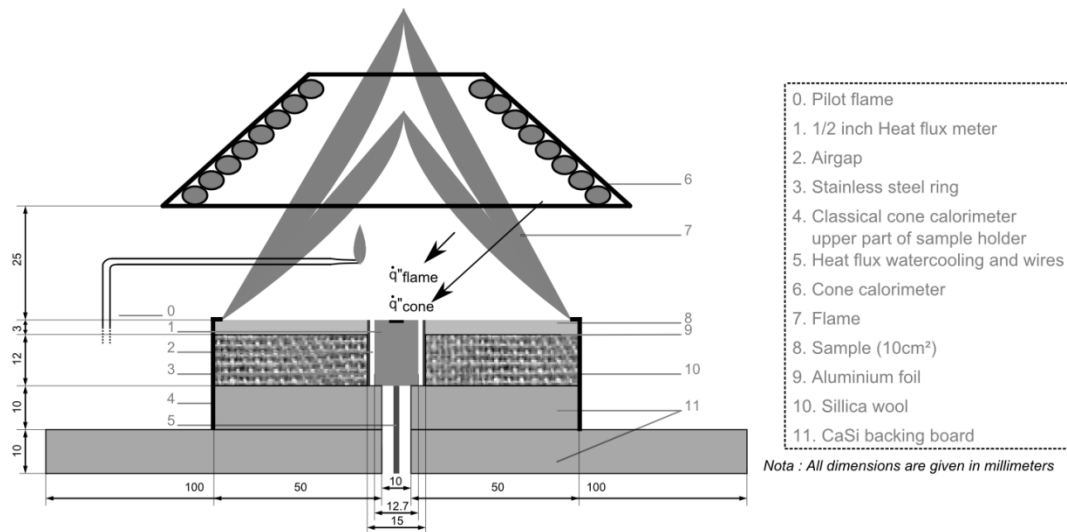


Figure 3: experimental setup used to measure flame heat flux in cone calorimeter

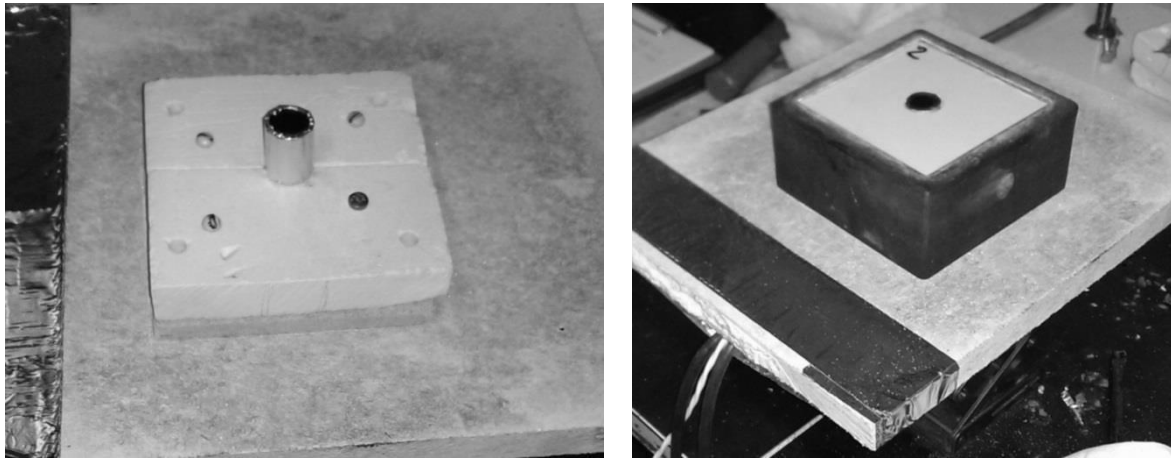


Figure 4: Pictures of the sample holder: empty (a) and ready for test (b)

4. Experimental results

As explained before, mass loss and gaseous products evolution were not collected during the tests. However, because of the similarity observed in the initial and final masses and in the time to ignition of the sample comparing to previously performed CACC test, the results of the measured flame heat flux will be jointly presented with already published results on the MLR of the ABS material [7] and with HRR results obtained during the same series of experiments but not published yet.

Figure 5 below shows the results obtained for the three heat fluxes considered. The curves presented have been chosen among others because they are the most representatives of the different trends. No particular treatments have been performed on the data. The curves presented are thus raw data obtained after conversion of the collected signal in mV to the heat flux in $\text{kW}\cdot\text{m}^{-2}$. Error on values is quite difficult to quantify, however, it is reasonably assumed to be inferior to 5% according to [17].

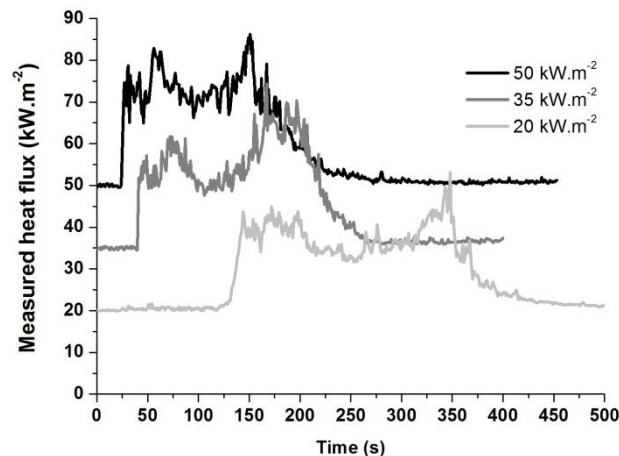


Figure 5: Evolution of the flame heat flux during cone calorimeter tests at different irradiance levels

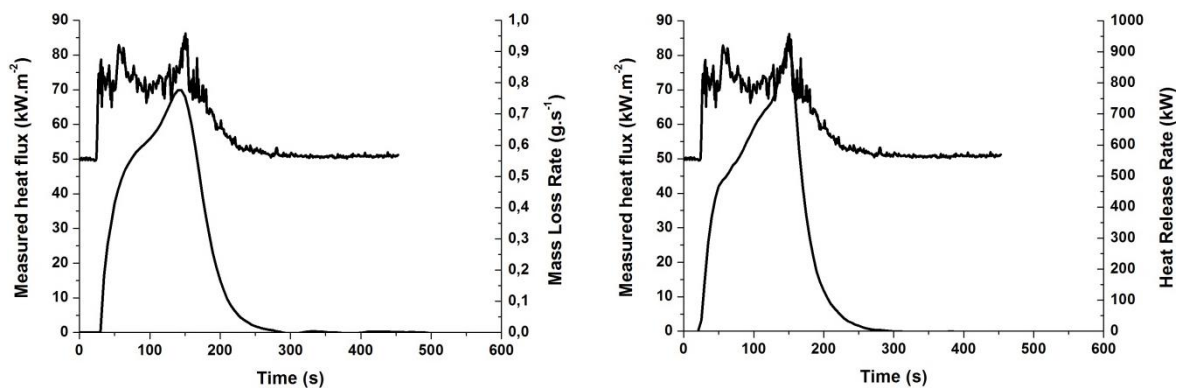
This figure highlights that the heat flux evolution can vary drastically all along the test. Indeed, for all three series, it can be seen that the first phase corresponds to a period during which the prescribed value of heat flux fixed at the beginning of the test is maintained constant. Then, ignition occurs at the surface of the material and a significant rise can be observed up to a first peak of heat flux. This first peak corresponds to the establishment of the flame at the surface of the material. Once well established, the heat flux value decreases for a time before reaching a second peak. This second peak of flux can be attributed to the chemical composition of the gaseous effluents. Suzuki & Wilkie [18] have proven that the gaseous compounds emitted during ABS's degradation are not released in equal quantities depending on the temperature. Those authors have highlighted that, as the thermal decomposition is initiated, butadiene is released and is the major flammable component which allows the apparition of the flame. With the flame appearance, temperature at the polymer's surface rises and aromatic compounds, especially styrene are released from the material. Aromatic gaseous compounds are then involved in the flaming process which has the effect of increasing greatly the energetic potency of the flame. Heat flux value fluctuates a lot after reaching this second peak, then decreases and stabilises reaching a

quasi-steady state (from 75 to 150s for the $50\text{kW}\cdot\text{m}^{-2}$ condition, 100 to 150s for the $35\text{kW}\cdot\text{m}^{-2}$ condition and 200 to 300s for the $20\text{kW}\cdot\text{m}^{-2}$ condition). Subsequently, the heat flux value increases again to reach a maximum value through a third peak which is due to the amount of combustible gaseous compounds emitted, which increases as temperature rises. Finally, the heat flux decreases until it reaches the reference heat flux fixed value at the beginning of the test. During this last phase, the flame is controlled by the amount of combustible gaseous compounds emitted by the thermal degradation process of the material, which rate is reduced progressively due to the lack of combustible. When the quantity of remaining combustible becomes too low, the flame decreases (in terms of height, luminous intensity and energy released) until it eventually is extinguished.

On the one hand, heat flux evolution kinetics attests that the heat flux reference value prescribed at the beginning of the test is reached and maintained, as long as no flaming process is associated with the thermal degradation of the samples. Besides, this reference heat flux is observed again at the end of the test. It should be noted that for the experiments described here, the prescribed heat fluxes were not exactly observed at the end of the test because of an experimental issue associated with the use of a cooled heat fluxmeter. It was observed that, during the tests, because of the cooling of the heat fluxmeter with cold water, gaseous compound emitted during the decomposition have condensed at the surface of the heat flux meter. This had the effect of perturbing the measurement. After every experiment, the initial value of the signal could only be observed after cleaning the surface of the heat fluxmeter. Figure 5 illustrates quite well this issue as the signal collected at the end of the test is always higher than the one collected at the beginning. Error is however relatively low, the biggest difference observed being in the magnitude of $2\text{kW}\cdot\text{m}^{-2}$. Nonetheless, this error can be avoided in using hot water to ensure the cooling of the heat fluxmeter. Rhodes [6] recommends heating the water used for the cooling higher than 65°C to avoid the condensation phenomenon. However, using hot water for cooling the heat fluxmeter requires to recalibrates the material.

On the other hand, the heat flux recorded at the surface of the material for all experiments is far higher than the test prescribed surface incident heat flux condition. These differences regarding peaks and mean values will be discussed later in the following sections. The presence of the flame enhances considerably the heat flux received at the surface whereas the cone calorimeter is not able to compensate thanks to the radiative spiral temperature regulation. It can be seen on Figure 5 that the establishment of the flame is faster when the heat incident flux imposed by the cone is higher. At high heat fluxes (*i.e.* 35 and $50\text{kW}\cdot\text{m}^{-2}$), the evolution of the heat flux to the first flux peak is reached quasi instantaneously, whereas the one reached at lower heat flux condition ($20\text{kW}\cdot\text{m}^{-2}$) is transient and much slower (approximately 10s). These results highlight that the higher the incident heat flux at the material surface quicker the establishment of the flame.

Besides, the shapes of the three different curves are similar, even if the degradation kinetics is modified. Because of the difference of the energy amount provided at the material's surface between the different tested conditions, degradation of the material occurs more or less swiftly. This trend is consistent with typical observations in a cone calorimeter when lowering the irradiance level imposed during the test. When plotting heat fluxes evolution curves jointly to MLRs and HRRs curves, it can be noted that the evolution of the heat flux have an important effect on the degradation kinetic of the ABS material, as seen in Figure 6. The slight time lag that can be observed between MLR and heat flux curves are due to the post treatment that have been performed on the MLR curves using moving average whereas heat flux curves haven't had any treatment.



a) Ignition time 21s

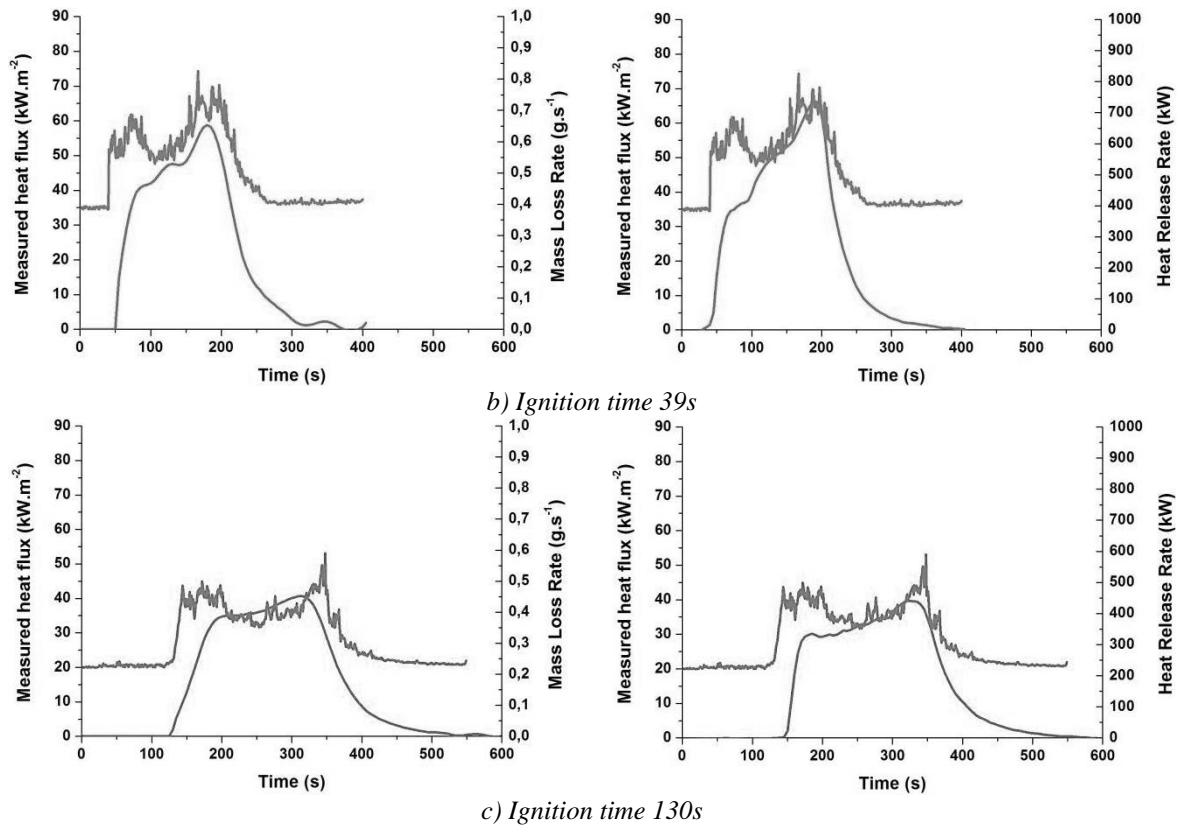


Figure 6: evolution of the heat flux received at the surface of the ABS material jointly plotted with MLR and HRR evolution at different heat fluxes (a) 50kW.m⁻², (b) 35kW.m⁻², (c) 20kW.m⁻²

For each tested condition, a complete analysis has been led to determine the total and relative value of the maximum heat flux reached, the total and relative mean of heat flux received during the tests and the total amount of heat flux due to the flame.

Table 3: Presentation of the maximums, means and total values of heat flux received by the material in the different tested conditions

	50kW.m ⁻²				35kW.m ⁻²		20kW.m ⁻²		
	Exp ₁	Exp ₂	Exp ₃	Exp ₄	Exp ₁	Exp ₂	Exp ₁	Exp ₂	Exp ₃
Maximum heat flux: total value (kW.m ⁻²)	88	90	85	86	77	74	52	53	54
Maximum heat flux: flame impact (kW.m ⁻²)	38	40	35	36	42	39	32	33	34
Mean heat flux on flaming duration: total value (kW.m ⁻²)	69	70	67	69	51	54	33	34	35
Mean heat flux on flaming duration: due to flame (kW.m ⁻²)	19	20	17	19	16	19	13	14	15
Mean of all tests: mean heat flux due to flame (kW.m ⁻²)	18.75 ± 1.26				17.5 ± 2.12		14 ± 1		
Heat flux ratio from flame (%)	27.3				33.5		41.2		
Total quantity of heat flux received due to the flame (area under curve) (MJ.m ⁻²)	3,6	3,4	2,9	4,1	3,7	4,2	2,7	4,4	4,8
Mean of all tests: Total quantity of heat flux received due to the flame (MJ.m ⁻²)	3.5 ± 0.49				3.95 ± 0.35		3.97 ± 1.15		

*Note: all exploitable results have been presented for all conditions

As highlighted in the first lines of Table 3, the maximum heat flux received at the material's surface is far higher than the one prescribed during the test. Indeed, the values recorded can reach from 180 up to 270% of the initially prescribed heat flux value (*i.e.* the heat flux condition imposed by the cone calorimeter at the beginning of the test). In particular, for the low prescribed heat fluxes, the heat flux provided by the flame can exceed the initially prescribed value. Nevertheless, this observation has to be considered carefully because it concerns only a very small period of time during the tests as they are peak values. Furthermore, the peak heat flux values functions of the test condition are quite similar as they extend from 33 to 42kW.m⁻² with a 37kW.m⁻² mean value.

Focusing now on the mean heat flux values collected, it can be seen in Table 2 that the heat flux attributed to the presence of the flame is in the same range for high heat fluxes (*i.e.* (18.75 ± 1.26) kW.m⁻² for 35kW.m⁻² prescribed and (17.5 ± 2.12) kW.m⁻² for 50 kW.m⁻² prescribed). For the low heat flux value tested (20 kW.m⁻²), it seems that a slight difference can appear because the value reached only (14 ± 1) kW.m⁻². Regarding the results, the hypothesis which implies that the flame heat flux is similar regardless the amount of incident heat flux before the appearance of the flame is questionable. There lies an interesting tendency which can provide useful information about the dependency or non-dependency of the flame heat flux to the imposed cone calorimeter heat flux which drives the degradation process. A hypothesis can be made regarding the results, which is related directly to the physical phenomenon occurring during the flaming process. As highlighted in [11] and [19], flame structure in a cone calorimeter can be divided in two parts: a fuel rich core where the gaseous emitted are in excess and a flaming area where this gaseous compounds mix with oxygen and are oxidized to form the flame. This is the part of the flame where exothermic reactions occur and emit energy in a radiative form. As the irradiance level imposed at the surface of the material increases, the amount of volatiles which emerge from the solid is increased and the fuel rich core volume as well as the flame volume increase greatly. Thus, the quantity of energy which is released in the flame and transmitted to the surface of the material is higher because of the increased volume of the flame area. The flame height is however limited and beyond a certain irradiance level imposed at the surface of the material it reaches its maximum height. This explains that the difference observed in terms of flame heat flux at the surface of the material is higher between 20kW.m⁻² and 35kW.m⁻² than between 35kW.m⁻² and 50kW.m⁻². Nevertheless, the quantity of results provided here cannot lead to an absolute conclusion and a much more complete experimental campaign would be needed to validate this.

The last part of Table 3 presents the summation of the total amount of heat flux received during the flaming process. It can be observed throughout the mean values presented that the results are very similar and do not depend on the experimentally fixed incident heat flux from the cone calorimeter. This trend provides useful information that completes the observations of the previous analysis. Indeed, even if this value is quite the same regardless the test condition, the period of time on which it is received is drastically different which highlights the differences observed between high and low heat flux in terms of mean flame heat flux.

Otherwise, as shown in Figure 7 a correlation can be established between the mean heat flux received and the mass loss rate during the flaming process. Indeed, this figure highlights the linearity of the mass loss rate function of the received amount of heat flux.

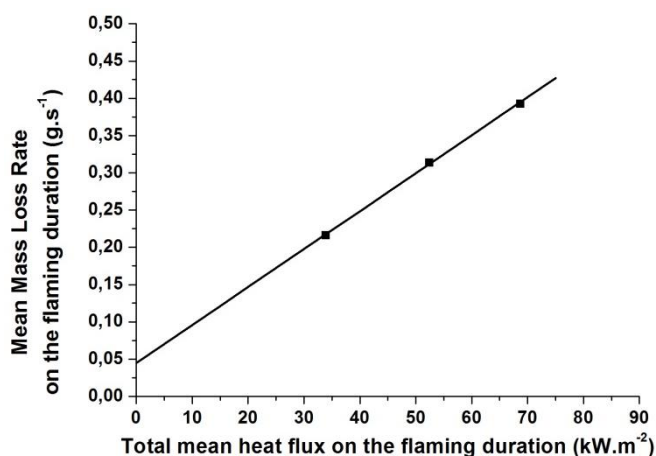


Figure 7: Mean MLR function of the total flame heat flux received at the surface of the material

Finally, the results presented in Table 3 are consistent with the literature values summarised in Table 1, even if this kind of results has never been obtained previously for an ABS material. However, the obtained results are in range of those obtained in other studies for similar polymeric materials.

5. Analytical review: experimental flame heat flux determination

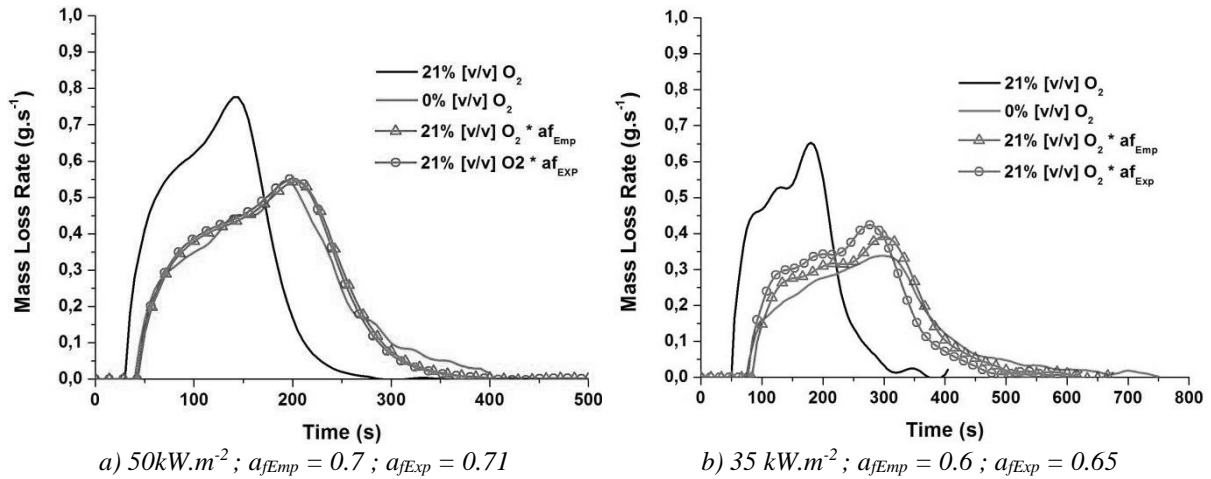
Now that the flame heat flux have been determined for the ABS material and for different considered heat fluxes, the analytical technic developed in the section 1 can be verified. In order to, the a_f coefficients can be recalculated with the following equation.

$$\overline{\dot{q}}_f'' * a_{fExp} = \dot{q}_{cone}'' \Leftrightarrow a_{fExp} = \frac{\dot{q}_{cone}''}{\overline{\dot{q}}_f''} \quad (3)$$

Where

- $\overline{\dot{q}}_f''$: Mean flame heat flux measured for the flaming duration
- \dot{q}_{cone}'' : Heat flux imposed at the material's surface by the cone calorimeter
- a_{fExp} : Experimental multiplier coefficient representing the amount of MLR due to the flame impact

Thanks to (3), a_{fExp} coefficients have been determined to be 0.71 and 0.65 respectively for the 50 and 35kW.m⁻² conditions. These values are consistent with the ones estimated in the first section (0.7 and 0.6). Once the a_{fExp} coefficients are obtained experimentally, they can be used to determine the effect of the flame heat flux on the MLR curves. The corrections of the coefficient values have been done on the curves presented in section 2 and the results are plotted on Figure 8.



a) 50kW.m⁻²; $a_{fEmp} = 0.7$; $a_{fExp} = 0.71$ b) 35 kW.m⁻²; $a_{fEmp} = 0.6$; $a_{fExp} = 0.65$
 Figure 8: Mass Loss Rate curves for ABS material at 21% [v/v] and 0% [v/v] oxygen concentration volume in controlled atmosphere cone calorimeter and modified curves using a_{fEmp} and a_{fExp} coefficient values

Obtained results illustrated by the figure above are quite in accordance with the ones found using the preliminary analysis. Indeed, concerning the 50kW.m⁻² condition, the a_f coefficient has remained almost unchanged. Besides, the coefficient found for the second studied conditions varied slightly. However it does not have an extreme impact on the results and the differences can be imputed to experimental and post treatment generated errors (filtering and smoothing).

6. Discussion and conclusion

Experimental measurements have been led to determine the flame heat flux in cone calorimeter for an ABS material. Several interesting observations have been drawn for this experimental campaign.

First and foremost, the results demonstrate that the evolution of the heat flux is similar in terms of shape regardless of the incident heat flux initially imposed at the sample's surface. Indeed, even if lowering the imposed irradiance level at a material's surface will delay its ignition time and slow down the establishment of the flame at its surface, the evolution of the heat flux remains the same. Ignition and flame establishment are related to ventilation conditions but above all to the presence of volatiles, the quantity of which is dependent on the amount of energy received by the material. It has been observed that, after ignition, the heat flux increases rapidly to reach a first peak, then decreases for a while until reaching a second peak which can be attributed to the energy released by the combustion of aromatic gaseous compounds such as styrene. Then the heat flux decreases and reaches a quasi-steady state before it increases again to reach a last peak, finally decreasing until

extinguishment of the flame. These results are otherwise in perfect accordance with the MLR and HRR parameters evolution.

Secondly, the heat flux during the test can be far higher than the prescribed one if indeed a combustion process is associated with the degradation of the material's condensed phase. Heat flux peak values reached can be twice as high as the test prescribed values. In terms of means, heat flux values can also be much higher than the prescribed values up by approximately 40%. Besides, it can be assumed that lower the prescribed heat flux, the higher the flame heat flux proportion.

This tendency proves that the heat flux generated by the flame seems to be dependant of the testing conditions even if slight differences were observed. Indeed, the flame heat flux mean values for the ABS material have been determined to be higher at high heat fluxes (35 and 50kW.m⁻²) than at low heat fluxes (20kW.m⁻²). This observation highlights that the energy emitted by the flame is linked with the quantity of reactions that occurs in the flame area. Indeed, as the quantity of emitted pyrolysis products increases and so the amount of reactions occurring in the flame it does affects its radiative potency.

In addition, these measurements have proven that a multiplier coefficient applied to the MLR results obtained in well ventilated environment can be used in order to predict the MLR under inert atmosphere. In the first place, this coefficient was determined empirically but the presented results have proven that it can also be calculated using the results of the flame heat flux measurement. The use of such a coefficient can be a great contribution in the field of computational fluid dynamics simulation. Indeed, knowing this coefficient could reduce or remove the need to perform numerous tests in multiple conditions to obtain data on material fire behaviour. Besides, results have proven that the use of such a coefficient is accurate between well ventilated and under-ventilated environments (*i.e.* 21% [v/v] and 0% [v/v] oxygen concentrations), but no information have been collected about the intermediate oxygen concentration values. Unfortunately tests haven't been performed at different oxygen concentrations. It is thus difficult to determine experimentally if a multiplier coefficient can be always used on MLR curves obtained in well oxygenated conditions to predict the MLR curves at any different oxygen concentration tested with the same prescribed heat flux. If this hypothesis was validated by means of complementary measurements, maybe it could be possible to determine a law governing the evolution of the coefficient and to prove (or disprove) its linearity.

Results obtained presents a real interest in demonstrating that the traditional use of cone calorimeter results throughout CFD codes is associated with an important error. Indeed, material kinetics which is supposed to correspond with a particular heat flux is in fact over-evaluated because of the differences between imposed heat flux and real impacted heat flux at the material's surface. This last point has been highlighted several years ago by the work performed notably at Maryland University by Rhodes, Quintiere and Hopkins [6], [20], [21] but also more recently [11], [13]. Although, even if the measurements performed within the experimental campaign are complex and time consuming, it could be interesting to perform other tests with different materials and in different conditions.

Finally, even if the total flame heat flux at the surface of the ABS material has been measured throughout this study, several shadow areas remain on the heat flux components. Among other things, attempting to determine a flame heat flux without considering the spectral aspect of the problem is questionable. Thus all the conclusions given here must be considered with caution because of the followings:

1. Material properties: in this study, the heat flux received by the material is referred as "incident". It has been so because of the lack of knowledge on the material spectral properties (absorbance and reflectivity depending on the wavelength). However, the key to a better understanding of the MLR variations is the absorbed heat flux within the material or at its surface. No experiments have been led to study the absorptivity of the material versus its reflectivity depending on the spectral distribution (*i.e.* it is impossible without performing further testing to determine either which part of the heat flux is absorbed or which part is reflected). It is however reasonable to think that the absorbance of the material can be drastically different from a spectral region to another.
2. Flame properties: no measurements were performed on the flame properties (soot quantity, emissivity, emittance, transparency, *etc.*). There is therefore a lack of knowledge on the phenomena occurring in flame, and its energy emittance could result of soot as well as radicals. Although, attributing the differences measured between prescribed and total heat flux received at the surface of the material to the flame is hazardous. As a simple example, after its establishment the flame can block a part of the heat flux provided by the cone and prevents it to reach the surface. This way, the heat flux provided by the cone heater would be overestimated and the one provided by the flame underestimated.

3. Heater properties: it has already been proven that the heater (i.e. cone calorimeter) radiative spectral emission is temperature dependant [22], [23]. Indeed, the wavelength distribution of the energy emitted by the heater changes slightly with the temperature. Thus, the energy absorbed by the material is dependant of the material absorptivity which depends on the wavelength of the emitted energy that can vary with the value of the prescribed heat flux of the cone calorimeter.

These last points highlight important perspectives, because determination of the absorbed heat flux (which is driving the decomposition process of the ABS material), requires further work on the determination of the spectral characteristics of the material, the radiant heat source and the flame. This opens up possibilities for future work that might be linked with recent works performed both on the radiative properties of cone calorimeter and materials [22] and on the radiative properties of flames [24], [25].

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