Radiative flux emitted by a burning PMMA slab

G Parent\textsuperscript{a}, Z Acem\textsuperscript{a}, A Collin\textsuperscript{a}, R Berfroi\textsuperscript{a}, P Boulet\textsuperscript{a,*}
Y Pizzo\textsuperscript{b}, P Mindykowski\textsuperscript{b}, A Kaiss\textsuperscript{b}, B Porterie\textsuperscript{b}

\textsuperscript{a} Université de Lorraine, LEMTA (UMR CNRS 7563), 2 av. de la Forêt de Haye, 54504 Vandoeuvre, France
\textsuperscript{b} Université de Provence, ETIC/ IUSTI (UMR CNRS 7343), 5 rue Enrico Fermi, 13453 Marseille, France

E-mail: pascal.boulet@univ-lorraine.fr

Abstract. The degradation of a PMMA sample has been studied based on experimental results obtained for the radiation emission by a burning slab. Observations of the infrared emission perpendicular to the plate, in the range where the optically thin flame is weakly emitting, indicate a plate temperature close to 680 K which is an indication on the surface temperature during the degradation process. Observations from the side allow a flame characterization without the plate emission superimposition. This is a promising way for evaluating data regarding the flame characteristics: temperature, gaz concentration and soot volumetric fraction.

1. Introduction

The degradation of materials is a key problem for studies dedicated to fire modeling as it provides the source terms as input data for the simulations, in particular regarding the heat transfer problem. All possible materials have been studied in the past decades, but there is a special one which receives a constant attention, being considered as an academic case: the Poly Methyl Methacrylate (or PMMA). PMMA is a non-charring material. It is also well-known to produce a stationary and slow degradation, which allows a good repeatability of the experiments aimed at characterizing its degradation and burning. A recent study on the degradation and the combustion of PMMA has been conducted by Pizzo et al. among others \cite{1, 2}. Starting from experimentations carried out on a burning vertical sample, models have been derived for the degradation, the boundary layer flow and the combustion itself. The experimentation was particularly focused on the sample itself, but owing to the stable and well-developed flame which was generated by the PMMA combustion, it appears that a fine spectral characterization of the flame can yield useful information about flame properties. On the other hand, recent investigations have been conducted on the emission of flames using fine spectral measurement in the infrared (see \cite{3, 4} for example). The flame characterization was conducted on vegetation fires, with inherent difficulties for the characterization of the fuel. Such emission study is applied here on a burning solid material for the first time, taking benefit of the stable behaviour of PMMA such as to provide reference data for the characteristic temperatures and intensities for this material. Then, the characterization in the infrared range can be useful for better understanding the degradation and better quantifying the products of the burning slab and heat fluxes generated by the combustion.
One justification of the present work is that radiative transfer is well-known to be of major importance for the fire propagation. This can help to better quantify the respective role of the soot and the combustion gases in the global flame radiation. This can also provide data for the solid fuel emission itself. The evaluation of the plate temperature is particularly difficult to achieve with confidence. Thermocouples can be used but this technique has unavoidable measurement biases which are difficult to evaluate. In the present study, radiation emission can be used such as to give an idea of the temperature through pyrometry-like measurements.

The degradation of a burning PMMA slab has been studied here for various sample sizes and considering emission perpendicular to the slab and from the side. The characterization of the radiative flux emitted in the infrared has been quantified for both the slab and the flame established at the surface. Then, a tentative identification of the flame characteristics has been carried out.

The paper is organized as follows: the experimental setup is briefly described, the results are commented for data obtained with a spectrometer and an IR camera, finally results are post-processed and commented for a specific flame characterization.

2. Experimental setup
For the present work, a device designed by the group ETiC/IUSTI has been used, involving a vertical slab (50 cm high, 20 cm wide and 3 cm thick) (see Figure 1). For each experiment, the sample is ignited at the bottom using a 2-kW electrical stainless steel rod (visible on the left hand side figure). The advantage of using this reference material (PMMA) is twofold: it is a noncharring material and it provides a stable steady flame (middle picture) during more than 20 minutes, with an excellent repeatability [1]. The flame and the plate are emitting radiation which can be analysed in order to obtain some information related to the degradation and the flame.

Radiation emission has been quantified here using a FTIR spectrometer (MATRIX by BRUKER) combined with a multispectral IR camera (FLIR Orion SC7000) thanks to a beamsplitter which separates the flux toward both apparatuses. Such combination was already used for flame characterization in [3]. In the present application it provides a complementary observation with spectra provided in the range [1.6-10 μm] thanks to the spectrometer, for a given position on the slab (a central area is observed corresponding to a circle with diameter 6 cm) and IR images with the camera at three definite wavelengths, for the whole slab. The selected...
wavelengths correspond to three filters with transmittance bandwidths centred at 2.85 µm for the first filter (for an observation of a part of the emission specifically attributed to H$_2$O), at 4.45 µm for the second one (for an observation of the CO and CO$_2$ emission) and at 3.9 µm for the last one (where no emission by the gases is expected to occur, the corresponding emission being attributed to the soot which is known to emit on the whole wavelength range in the infrared). Data are post-processed thanks to a calibration step carried out with a high temperature blackbody (Mikron M330 EU) as already presented in [3, 4]. On Figure 1 the measurement apparatus is visible on the right hand side figure where the plate is observed from the side in a configuration which allows to study the flame emission without the superimposition of the plate emission. By varying the plate width, one can observe flames of various widths. In the present study, plates 5, 10 and 20 cm in width have been used, providing flames with quite the corresponding widths. The observation of the emission can be done also perpendicularly to the plate. In this case, the radiation received by the apparatus is the combination of the emission by the plate plus the emission by the flame itself. In the present study, such observation perpendicular to the plate is carried out for the 20 cm wide plate. Both observation situations - perpendicular and lateral configurations - will be discussed below.

3. Experimental results
3.1. Spectroscopic data
Results obtained with the spectrometer are commented first. Figure 2 presents the radiation emitted in steady conditions perpendicular to the plate, meaning emission by both the slab and the flame, after conversion of data into intensity. Twelve spectra are plotted on the figure, corresponding to acquisitions performed successively (time after ignition indicated in the caption), starting 4 minutes after the ignition in order to ensure that the stationary regime is reached (the flame is developed, involving the whole plate at this step as shown on the middle picture of Figure 1). The very good repeatability of the measurement is obvious since the curves are superimposed, yielding one single curve.

Regarding the spectral shape of the emission, there is a strong peak around 2300 cm$^{-1}$ which is usually attributed to CO and CO$_2$ emission. A second hot gas characteristic emission is seen below 2000 cm$^{-1}$ and in the range [3400-4200 cm$^{-1}$] due to water vapour. Then, there

Figure 2. Emission spectra by the burning plate in stationary regime
is a continuous emission which can be attributed to the emission by the plate (which in this range is not far from being a black surface, according to [5]) and possibly to soot produced in the flame. This assumption of a near black behaviour of the plate may seem questionable, but for a plate 3 cm thick of raw clear PMMA Forsth and Roos [5] suggest values close to 0.91-0.93 for the average absorptivity (in the wavelength range of interest, considering the flame spectrum). Moreover, the degradation visibly produces a black deposit on the surface when the sample is observed during the experiment, which is expected to further increase the sample absorptivity, making the assumption of a black surface behaviour a good estimation. In a next study, a correction accounting for the reflectivity could be introduced in order to perform a better quantitative analysis.

An indication on the emission level is suggested by the dashed lines on the figure, which correspond to Planck’s curves for blackbodies at 1105 K and 684 K respectively. The temperature 1105 K provides the maximum intensity observed for the hot CO\textsubscript{2} emission. Of course this is only an equivalent temperature and the gas temperature is assumed to be higher since the flame is optically thin and its emissivity is lower than 1. The value 684 K yields the best fit (using a least square method) which provides the same emission level for the continuous background aside the gas peaks. Assuming an optically thin flame on the one hand (which will be also discussed below through IR images) meaning a weak emission by the soot, and a plate emissivity close to 1 on the other hand, this 684 K value is close to the surface temperature where the degradation occurs.

3.2. IR images

IR images are now studied, still for an observation perpendicular to the plate. Figure 3 presents IR images in terms of intensity on the left and equivalent temperature on the right (the temperature of the blackbody which would provide the same intensity as the measured one). Contrary to the previous comments which concern the whole spectrum but are restricted to the central area of the plate, results are now commented on definite wavelengths but the whole plate can be observed. From the top to the bottom, figures correspond to the emission at 4.45 \(\mu\text{m}\) or 2250 cm\(^{-1}\) (a wavelength where hot CO\textsubscript{2} produced by the combustion is strongly emitting), at 2.85 \(\mu\text{m}\) or 3500 cm\(^{-1}\) (a wavelength where hot H\textsubscript{2}O is emitting) and at 3.9 \(\mu\text{m}\) or 2560 cm\(^{-1}\) (a wavelength where there is no emission from hot gases, so that only the slab and soot contributions can be seen). The flame structure appears in the foreground to the plate emission, especially on the results presented in terms of intensity, but also through the equivalent temperature plots. White circles near the plate center indicate the area which was observed by the spectrometer. In an average sense, intensity values observed in this area are higher for the CO\textsubscript{2} contribution in accordance with those obtained with the spectrometer and commented in the previous section.

Results converted in temperature (right hand side figures) show a background below 700 K with hotter structures which correspond to the flame influence. The bottom right figure is the best suited for the evaluation owing to its scale. In the same time, this confirms the weak contribution of soot as the flame influence in front of the plate is hardly visible. One can note that this background contribution is quite homogeneous. As above explained this provides a temperature close to a realistic one because the flame emission itself is weak in the infrared and because the plate surface is near black. This is also evidenced by the fact that the same background temperature is indicated whatever the studied wavelength (meaning negligible soot contribution and no relevant plate emissivity modification). On the contrary the light structures revealing the flame exhibit equivalent temperatures which are weaker than the true temperature of the gas since the flame emissivity is probably far from 1.

A finer evaluation has been done regarding the average temperature of this background emission, considering the exact grey level and the calibration data. A value of 670 K has been
Figure 3. IR images with the different filters, in terms of intensity in W/m²sr.cm⁻¹ (left) and equivalent temperature in K (right)
found which best represents the intensity level. Recalling the spectroscopic analysis of the previous section, this represents a discrepancy of 2% as compared to the 684 K observed above. This confirms the value of the degradation temperature of the burning PMMA at the surface sample.

4. Flame characterization
The previous section has produced an information on the sample surface temperature but the flame cannot be easily isolated for a specific characterization in this configuration perpendicular to the plate. Therefore a second observation from the side has been carried out with the camera in order to obtain the emission from the flame solely (the spectrometer cannot be used here as it would observe a too large area, receiving radiation from the flame but also from the plate side and the background behind the burning plate). The camera observations have been done for plates - and consequently flames - of different widths. The underlying idea is to obtain an evolution of the emission as a function of the flame width, allowing the evaluation of the intrinsic property of the flame such as its absorption coefficient.

Figure 4 presents the applied method and the typical results obtained after post-processing. The IR image of the flame is first presented on the left, for the case of a 10 cm wide flame, in the H$_2$O emission range. Three points are chosen for a quantitative evaluation, indicated by the white spots in Fig. 4 (approximately 12, 20 and 45 cm from the leading edge of the flame). Then, the intensity level for these three points is registered as a function of time in order to extract an average value. This method is used for the three plate widths, finally providing the plot presented in Fig. 4.

Three colors are chosen for discriminating the flame width influence (indicated on the figure with the dashed line). As it could be expected, the intensity level rises with the flame width. Then, three curves are plotted for each width, corresponding to the three locations in the flame (bottom, middle and upper positions). It must be pointed out that the mean behaviour is similar whatever the location in the flame. There is a fluctuation in the intensity due to the flickering behaviour of the flame, but, in average, the local intensity is the same whatever the

![Intensity for the 10 cm wide plate](image1)

![Intensity level for the three positions](image2)

**Figure 4.** Intensity level at 3500 cm$^{-1}$ (H$_2$O emission range) at three positions in the flame. The plate is observed from the side. On the left: intensity distribution for the 10 cm plate. On the right: intensity level as a function of time for the three locations indicated by white spots on left hand side figure, for the three plates 5, 10 and 20 cm in width.
Figure 5. Fit of emission data for the evaluation of the flame absorption coefficient

location. Beside the flickering behaviour, a stable average value appears, which also explains why the spectra (which correspond to a spatial average on a circle with a 6 cm diameter as above explained) exhibit good repeatability.

A further analysis can be carried out to estimate the typical absorption coefficient of the flame, assuming a standard form for the flame emission as follows

\[ I = I_b(T) \cdot \left[ 1 - e^{-\kappa E} \right] \quad (1) \]

where \( I, I_b, T, \kappa \) and \( E \) stand for the intensity emitted from the flame toward the detector, the blackbody intensity at temperature \( T \), the flame temperature, the absorption coefficient and the flame width respectively. It must be emphasized that the use of such a formulation for the flame property identification would require a fine description of the spectral properties of the gases, like a line by line calculation, because of well-known problems of spectral correlation when considering gas properties averaged on definite bands. This is beyond the scope of the present preliminary study. Therefore, the following analysis should be considered as an approximated evaluation, especially in what concerns the gas characteristics.

The absorption coefficient can be evaluated, provided the flame temperature is known. This is another problem here which makes the present analysis rather exploratory than quantitative, but we go ahead in order to see if the method could be applied. The choice of the temperature of 1105 K is done, following the curve plotted on Figure 2 that best fits the maximum emission. An average value is first obtained from the right hand side part of Figure 4. Then, Figure 5 presents the result of \( \ln \left( \frac{1}{1 - I/I_b} \right) \) as a function of the flame width. The expected linear behaviour is obvious. Despite some uncertainties (further verifications must be conducted in order to check the accuracy), one can identify the slopes for each wavelength, finally suggesting the absorption coefficients of the present PMMA flame, given in Table 1. Values are in a correct range, but a true validation is difficult due to a lack of data, especially for this non typical flame.

Regarding the soot contribution, if a simple model as the usual one reported in [6] is used

\[ \kappa = \frac{5.5 f_v}{\lambda} \quad (2) \]

where \( f_v \) stands for the soot volume fraction and \( \lambda \) for the wavelength, an evaluation of the volumetric fraction can be performed. A value of \( 3.5 \times 10^{-7} \) m³/m³ is obtained for the present
case. Again this is a value in accordance with usual data for such material but few reference values are available to our knowledge for a real validation. Pagni and Bard mention a value of $3.1 \times 10^{-7}$ m$^3$/m$^3$ for black PMMA, which is in close agreement with the present value [7].

This shows that a further analysis could be carried out with a similar method, aimed at quantifying the soot and gas concentrations in the flame, together with a more accurate flame temperature. This will be the focus of a future work, ensuring an optimal identification by using genetic algorithm like-methods for example, which will allow the simultaneous identification of all the studied variables.

5. Concluding remarks

The emission by a PMMA plate has been characterized experimentally combining a setup aimed at studying the ignition and the burning of a PMMA vertical plate and a method for the characterization of the emission in the infrared range. The spectra emitted by the burning plate show emission by hot gases in the flame and a continuous background which can be attributed to the plate and the soot in the flame. However, the flame is optically thin and the soot contribution is almost negligible in the infrared range. The plate which is supposed to be quite a black surface has been observed to have a temperature between 670 and 684 K owing to the two methods used for its characterization. By studying the produced flame itself, the different contributions of CO$_2$, H$_2$O and the soot have been observed, providing typical absorption coefficients of the flame at three characteristic wavelengths. An extension of this method in order to identify a soot volumetric fraction has been tested. A representative value of $3.5 \times 10^{-7}$ m$^3$/m$^3$ has been obtained which is in accordance with the expected order of magnitude for such case. Further analysis could be applied with the present identification method as to yield a soot distribution based on the acquired IR images. Similar identification could be sought also for the combustion gases, introducing a fine radiation model for the gases, like a line-by-line model for example. Such characterization will be the aim of a future work, before application of the present analysis to other materials.

References
[1] Pizzo Y, Consalvi J, Querre P, Coutin M, Audouin L, Porterie B and Torero J 2008 *Combustion and Flame* **152**(3) 451
[2] Pizzo Y, Consalvi J, Querre P, MCoutin and BPorterie 2009 *Fire Safety Journal* **44** 407
[3] Boulet P, Parent G, Acem Z, Porterie B, Kais a A, Billaud Y, Pizzo Y and Picard C 2011 *Journal of Combustion* 2011 Article ID 137437
[4] Boulet P, Parent G, Collin A, Acem Z, Porterie B, Clerc J, Consalvi J and Kais a A 2009 *Int. J. Wildland Fire* **18** 875
[5] Forsth M and Roos A 2010 *Fire materials* DOI: 10.1002/fam.1053
[6] Modest M 2003 *Radiative transfer, 2nd Ed.* (Academic Press)
[7] Pagni P and Bard B 1978 *Proc. Seventeenth Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, Pennsylvania) p 326