Influence of the Oxidizing Temperature on the Combustion of Some Well-Known Polymeric Materials

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Synopsis

The purpose of this work is to characterize the combustion of little samples of some well-known polymeric materials, polyethylene, polypropylene, and polystyrene, in an atmosphere of quiescent hot air at different temperatures. The analytical treatment of this problem, which is a heat and mass transfer one with chemical reaction between pyrolysis and oxidizer gases, is based upon the fact that the burning regime is diffusion controlled. A mathematical approach developed from Spalding's theory, taking into account radiative effects, is applied to this model of combustion. Experimental results allow us to determine the apparent heat of combustion of these different materials and to study the evolution of radiative and convective fluxes.

INTRODUCTION AND SCOPE

The generalized utilization of polymeric materials in every day life sets a crucial problem of security as far as fire prevention is concerned.

Consequently, this very important problem requires a sustained effort to obtain a better understanding of the combustion of these materials, especially for different types of configurations and different oxidizing environments.

It is generally observed that these factors greatly influence the rate of combustion, and it is now well established that the dominant heat transfer process is radiative in nature for large-scale fires and convective for small-scale laboratory fires.

The main purpose of this work is to study the combustion of little samples of some well-known polymeric materials, polyethylene (PE), polypropylene (PP), and polystyrene (PS), in a reactor containing quiescent hot air at different temperatures.

It is well known that the flame established near the surface of a combustible material is a diffusion flame. As a result of the heat transfer, the solid undergoes pyrolysis and gives combustible gases, which diffuse into the air. The reactants are supposed to react instantaneously in the flame zone.

The combustion may be described by means of Spalding's theory.^{1,2} Nevertheless, the experimental configuration requires that radiation exchanges between the walls of the reactor and the surface of the material must be taken into account and added to radiative effects of the flame.

Then it is possible to establish the relative importance of fluxes of different nature, giving rise to the gasification of the material, and to show a heat blocking effect resulting from the augmentation of mass flux due to radiation, which decreases the net convective heat flux.

THEORETICAL STUDY

The analytical treatment of a heat and mass transfer problem with chemical reaction between pyrolysis and oxidizer gases is based upon the fact that the burning regime is diffusion controlled.

In the diffusion flame, the chemical reaction occurs infinitely fast. A distinct and infinitesimally thin reaction zone separates the fuel from the oxidizer. This means that no oxidant is present on the fuel side of the flame and no fuel on the other side. At the "flame shell" fuel and oxidant concentrations are zero.

The burning rate, measured from the consumption of the material depends on thermodynamic and aerodynamic factors.

In our field of interest the combustion of the samples is studied in an enclosure, and the influence of its temperature on the burning rate is examined.

This influence occurs in two ways: it affects the convective heat transfer term which depends on the gas phase temperature gradient; it is necessary to introduce a radiative term accounting for the radiative effect of the wall in addition to the radiant fluxes from the flame to the material surface.

To characterize the radiative effect, the theoretical scheme is modified by using a method derived from Fineman's method.³

The studied samples are small cubes which soften under the influence of heat and take a hemispheric shape. Consequently, the conservation equations are used in spherical coordinates, r being the coordinate normal to the polymer surface.

Some simplifications are made. The thermal and thermochemical properties and time-averaged variables are considered constant. Specific heats, thermal and mass diffusivities of all the gas-phase species are supposed to be equal.

The conservation equations are the following:

Continuity, i.e. conservation of mass:

$$m_s \cdot r^2 = \text{const.} \tag{1}$$

This equation implies that the total rate of mass transfer $(m_s 2\pi r^2)$ remains constant and equal to the value at the surface $(m_s 2\pi R^2)$.

Energy:

$$k_{g}r^{2}\frac{d^{2}T}{dr^{2}} - C_{p_{g}}m_{s}r^{2}\frac{dT}{dr} + r^{2}\frac{dq_{r}}{dr} + r^{2}Q = 0$$
(2)

Species:

$$\rho_g D_g r^2 \frac{d^2 y_i}{dr^2} - C_{p_g} m_s r^2 \frac{d y_i}{dr} + r^2 W_i = 0 \tag{3}$$

where k_g , C_{ρ_g} , ρ_g , and D_g are the gas-phase thermal conductivity, specific heat capacity, density, and diffusion coefficient, respectively, m_s is the mass flux, y_i is the species *i* mass fraction, q_r is the radiative heat flux, dq_r/dr is the radiative source per unit volume per unit time, and Q and W_i are the volumetric heat and species source-sink terms, respectively.

Chemical reactions are assumed to occur infinitely fast at stations where fuel vapor and oxygen are present in stoichiometric proportions resulting in an extremely thin flame sheet.

The fast, simple, single-step stoichiometric relation

 $i \text{ kg of fuel} + 1 \text{ kg O} \rightarrow (1 + i) \text{ kg of product} + i \Delta H_c \text{ J}$ leads to the following relations among sources and sinks:

$$\frac{W_F}{i} = W_0 = -\frac{Q}{i\Delta H_c} \tag{4}$$

where i is the fuel/oxygen stoichiometric mass ratio.

The heat fluxes transferred to the surface are both convective and radiative in nature. Our experimental configuration leads to consider a radiative heat flux from the walls as well. Besides, the flame sheet is assumed to radiate as an optically thick gray body at a temperature T_f , and the fuel side and the air side of the flame sheet are assumed to be occupied by gases which do not contribute to the flame radiation by either emission or extinction; under these conditions the radiative flux source term that ought to be present in eq. (2) vanishes due to this assumption of nonparticipating space on either side of the flame and the surface energy boundary condition is

$$m_s \cdot \Delta H_g = k_g \left. \frac{dT}{dr} \right|_s + q_r \tag{5}$$

where ΔH_g is the overall latent heat of gasification of the material and q_r the radiative flux to the surface.

The boundary conditions associated with species conservation at the fuel surface take the following form similar to (5):

$$m_s = \rho_g D_g \frac{d}{dr} \left(\frac{y_F}{y_{F_s} - 1} \right) \tag{6}$$

where the fuel mass fraction at the surface y_{F_s} is related to the temperature of surface T_s via pyrolysis kinetic laws.

The losses suffered by the flame towards the ambience as well as the material and the completeness of the combustion tend to reduce the flame temperature to some extent. This reduction is merely accounted for by defining an apparent heat of combustion $\Delta H_c^* = \Delta H_c (1 - \gamma)$, where ΔH_c is the true heat of combustion and γ a coefficient corresponding to the losses and to incompleteness of the reaction.

Combining eqs. (1)-(6) and eliminating the sources and sinks terms, we can obtain the expression of the burning rate

$$m_s = (\rho_g D_g/R) \ln (B+1) \tag{7}$$

where B is the mass transfer driving force defined as

$$B = [C_{p_g}(T_{\infty} - T_s) + \Delta H_c(1 - \gamma)iy_{0\infty}]/\Delta H_g(1 - E)$$
(8)

with

$$E = q_r / (m_s \cdot \Delta H_g) \tag{9}$$

and the expression of the apparent heat of combustion

$$\Delta H_c (1 - \gamma) = \{(1 + iy_{0\infty}) [C_{p_g}(T_f - T_s) + \Delta H_g(1 - E)] - \Delta H_g(1 - E) - C_{p_g}(T_\infty - T_s)\}/iy_{0\infty} \quad (10)$$

These expressions are used for the correlation of our experimental results. We can consider the material samples as small gray surfaces at temperature T_s in a gray enclosure of great size at temperature T_w and in this case the radiative heat transfer can be written as

$$q_{r_w} = \epsilon_s \,\sigma(T_w^4 - T_s^4) \tag{11}$$

where ϵ_s is the emissivity of the solid surface and σ the Stefan–Boltzmann constant.

It is experimentally possible to determine the evolution of the wall temperature T_w vs. the reactor temperature T_{∞} .

Since the variation of T_s with surface regression rate is very weak, negligible error will be introduced in an analysis of a steady burning case if it is assumed that the surface temperature does not vary with regression rate.

Moreover, the sample is surrounded by a conical flame at temperature T_f . This flame radiates to the surface without altering the radiative exchange wall surface. In effect, the emissivity of the flame ϵ_f is very weak as well as its absorptivity.

We can estimate the total radiation leaving the flame by

$$q_{r_f} = \sigma \epsilon_f T_f^4$$

The emissivity of the flame $\epsilon_f = 1 - e^{-KL}$, where K is the absorption emission coefficient and L the mean beam length, is reduced to $\epsilon_f = KL$ in the case of a thin flame with $KL \ll 1$.

Hence we have

$$q_{r_f} = \sigma K L T_f^4$$

The value of L depends both on the shape of the flame and on the place where the flux is determined. Generally its evaluation is not easy. Nevertheless, it may be merely evaluated considering the flux emitted by a flame of specified shape to a particular location on the sample. Modak⁴ has provided a model allowing to determine analytically the radiative flux from an optically thin conical flame to the center of the sample of radius R.

The optically thin mean beam length is given by

$$L = 2R \left[1 + \frac{h-1}{h^2 + 1} - \frac{h^2}{(h^2 + 1)^{3/2}} \ln \left(\frac{h\sqrt{h^2 + 1} + h^2}{\sqrt{h^2 + 1 - 1}} \right) \right]$$
(12)

with H_c height of the cone and $h = H_c/R$ nondimensional height of this cone.

The radiative balance at the surface is the following:

$$q_r = q_{r_w} + q_{r_f} = \epsilon_s \sigma (T_w^4 - T_s^4) + \sigma K L T_f^4$$
(13)

According to the values of the different temperatures $(T_w, T_s, \text{ and } T_f)$, the balance may either be positive [radiative flux contributes to the gasification and the ratio E given by (9) is positive] or negative (the sample loses radiative energy and E is negative). From this total radiative heat flux, we can obtain the convective heat flux

$$q_c = \frac{\Delta m \cdot \Delta H_g}{2\pi R^2} - q_r \tag{14}$$

and study its variation with the reactor temperature. This variation allows to show up the relative importance of the radiative and convective fluxes and the "heat blocking" effect (the augmentation of the mass flux due to radiation decreases the net convective heat flux):



Fig. 1. Experimental apparatus.

EXPERIMENTAL AND RESULTS

The apparatus is shown in Figure 1. It is derived from that setup in the Laboratory to study autoignition delays and limits.^{5,6} It consists of a cylindrical stainless steel reactor heated by coils imbeded in a refractory cement. The temperature is monitored by an electronic device using a 0.1 mm Chromel-Alumel thermocouple as a sensitive element.

In the middle part of this reactor we have two apertures: the first is fitted with a window, and the second allows the passage of the sample holder which is fixed to the reactor by means of a joint through which it can slide.

The experiments were carried out with 50 mg polymer samples in quiescent air. They are ignited using a small diffusion burner flame and are rapidly introduced in the reactor previously maintained at a fixed temperature.

Then we allow them to burn during a specified time. The burning rate is obtained from the mass loss during this combustion time.

If Δm is the mass loss measured per unit time for a surface sample $2\pi R^2$ (the samples are assumed to be hemispheres of radius R), the mass flux is

$$m_s = \Delta m / 2 \pi R^2$$

and eq. (7) becomes

$$\frac{\Delta m}{2\pi R^2} = \frac{\rho_s D_s}{R} \ln \left(B + 1\right)$$

On account of the lack of accuracy of this method, it is necessary to determine Δm with a great number of tests (10 or more).

The radius of the equivalent hemisphere is the initial radius what introduces only a little error as the mass loss is very small.

Results obtained are shown in Table I.

It is noticeable that the mass fluxes determined at ambient temperature are very near those of Delbourgo and Coll⁷ (respectively, 0.57×10^{-2} kg m⁻² s⁻¹ and 0.65×10^{-2} kg m⁻² s⁻¹ for polyethylene and polypropylene) with greater samples (2.1-cm rod).

Tewarson and Pion⁸ obtained greater values of mass flux $(1.6 \times 10^{-2} \text{ kg m}^{-2})$

	PE	PP	\mathbf{PS}	PE	PP	PS
<i>Τ</i> _∞ (°C)	Δn	$n \times 10^6$ (kg·s ⁻	-1)	$(\Delta m/2\pi)$	R^2) $ imes 10^2$ (kg	$-m^2-s^{-1})$
25	0.44	0.48	0.62	0.80	0.74	1.22
100	0.47	0.57	0.59	0.86	0.97	1.16
150	0.52			0.95		_
200	0.54	0.45	_	0.98	0.77	
300	0.62	0.50	0.69	1.12	0.86	1.35
400	0.69	0.58	0.78	1.25	0.99	1.53
450		0.68	_		1.16	
500	0.79		0.84	1.43	_	1.65
550	0.88	0.86		1.60	1.47	
600	0.99	1.10	1.34	1.80	1.89	2.62
650 •	1.22	1.37	1.61	2.22	2.35	3.16

TABLE I Burning Rates and Mass Fluxes of Different Polymeric Materials

s⁻¹ for polyethylene and polypropylene and 3.9×10^{-2} kg m⁻² s⁻¹ for polystyrene) with quite a different scale 30×30 cm pieces. As pointed out before, this is due to the difference in types of configuration and environment conditions.

The maximum temperatures measured at the tip of the flame (using a 25μ Pt/Pt-Rh thermocouple) are the following: 1300°C for polyethylene and polypropylene; 1050°C for polystyrene.

These values are very close to those usually encountered for these types of materials.

The evolution of the wall temperature with the reactor temperature is determined using a thermocouple (0.1 mm Chromel-Alumel) set against the wall. This evolution is exhibited in Figure 2.

EXPLOITATION OF RESULTS

It is quite informative to compare the burning properties of the different plastic fuels.



Fig. 2. Evolution of the wall temperature with the reactor temperature.

Data Summary for the Timee Materials				
Materials	Polyethylene	Polypropylene	Polystyrene	
Fuel/oxygen				
(stoichiometric ratio $i)$	0.29	0.29	0.32	
Surface temp				
$T_{s}(^{\circ}{ m C})^{7,9}$	480	480	430	
Overall latent heat of degradation				
$\Delta Hg \times 10^{-6} (J \cdot kg^{-1})^{8}$	2.17	1.99	1.79	
Theoretical heat of combustion				
$\Delta H_c \times 10^{-7} (J \cdot kg^{-1})$	4.37	4.36	4.01	
Absorption emission coefficient				
$K(m^{-1})^{10}$	1.8	1.8	5.3	

TABLE II Data Summary for the Three Materials

Apparent Heat of Combustion

The burning rates (Table I) and the flame temperatures measured at ambient T_{∞} allow us to determine the apparent heat of combustion. Then it is assumed that this apparent heat of combustion is a constant for a given polymer burning in air at different temperatures.

The apparent heat of combustion is determined using eq. (10). To use this equation it is necessary to know the radiative contribution to the surface energy balance:

$$E = \frac{q_r}{(\Delta m \cdot \Delta H_g)/2\pi R^2}$$

Equation (13) gives q_r . Table II provides a summary of the three materials data.

For the emissivity of solids we used the allowed value of 0.9. The specific heat C_{p_g} gas phase may be assumed as constant equal to 1.25×10^3 J·kg⁻¹ K⁻¹; for



Fig. 3. Evolution of radiative flux leaving the flame in function of temperature for the different values of K: (\bullet) 1.8 m⁻¹ (polyethylene and polypropylene); (O) 5.3 m⁻¹ (polystyrene).

						· · · · · · · · · · · · · · · · · · ·	- <u> </u>
$\frac{T_w}{(^{\circ}C)}$	T_{f}	$q_{r_w} = \\ \sigma \epsilon_s (T_w^4 - T_s^4)$	$- q_{r_f}$ $\cdot 10^{-4}$ (V	$\frac{q_{r_w} + q_{r_f}}{W \cdot m^{-2}}$	$\Delta m \cdot \Delta H_{g/}$ $2\pi R^2$	/q	E defined by eq. (9)
	· · · · ·	·····		, ,			eq. (e)
25	1300	-1.59	0.17	-1.42	1.71	3.13	-0.83
100	1371	-1.55	0.21	-1.34	1.84	3.18	-0.73
152	1439	-1.46	0.25	-1.21	2.05	3.26	-0.59
205	1495	-1.38	0.29	-1.09	2.13	3.22	-0.51
317	1615	-1.00	0.38	-0.62	2.42	3.04	-0.26
428	1742	-0.42	0.46	0.04	2.72	2.68	0.15
545	1879	-0.63	0.63	1.26	3.09	1.83	0.41
608	1953	1.42	0.71	2.13	3.47	1.34	0.61
680	2028	2.55	0.84	3.39	3.89	0.50	0.87
730	2083	3.51	1.04	4.55	4.81	0.26	0.95
	$\begin{array}{c} T_w \\ (^{\circ}C) \\ 25 \\ 100 \\ 152 \\ 205 \\ 317 \\ 428 \\ 545 \\ 608 \\ 680 \\ 730 \end{array}$	$\begin{array}{c c} T_w & T_f \\ \hline (^\circ C) \\ \hline 25 & 1300 \\ 100 & 1371 \\ 152 & 1439 \\ 205 & 1495 \\ 317 & 1615 \\ 428 & 1742 \\ 545 & 1879 \\ 608 & 1953 \\ 680 & 2028 \\ 730 & 2083 \\ \hline \end{array}$	$\begin{array}{c c} q_{r_w} = \\ \hline T_w & T_f \\ \hline (^{\circ}\mathrm{C}\mathrm{C}\mathrm{)} \end{array} \qquad \begin{array}{c} \sigma \epsilon_s (T_w^4 - T_s^4) \\ \hline \sigma \epsilon_s $	$\begin{array}{c c} q_{r_w} = \\ \hline T_w & T_f \\ (^{\circ}\mathrm{C}\mathrm{C}\mathrm{)} & \hline \sigma\epsilon_s(T_w^4 - T_s^4) & q_{r_f} \\ \hline 25 & 1300 & -1.59 & 0.17 \\ \hline 100 & 1371 & -1.55 & 0.21 \\ \hline 152 & 1439 & -1.46 & 0.25 \\ 205 & 1495 & -1.38 & 0.29 \\ 317 & 1615 & -1.00 & 0.38 \\ 428 & 1742 & -0.42 & 0.46 \\ 545 & 1879 & -0.63 & 0.63 \\ 608 & 1953 & 1.42 & 0.71 \\ 680 & 2028 & 2.55 & 0.84 \\ 730 & 2083 & 3.51 & 1.04 \\ \end{array}$	$\begin{array}{c c} q_{r_w} = & \\ \hline T_w & T_f & \sigma\epsilon_s(T_w^4 - T_s^4) & q_{r_f} & q_{r_w} + q_{r_f} \\ \hline (^{\circ}\mathrm{C}\mathrm{C}\mathrm{)} & & -1.59 & 0.17 & -1.42 \\ \hline 100 & 1371 & -1.55 & 0.21 & -1.34 \\ \hline 152 & 1439 & -1.46 & 0.25 & -1.21 \\ 205 & 1495 & -1.38 & 0.29 & -1.09 \\ 317 & 1615 & -1.00 & 0.38 & -0.62 \\ 428 & 1742 & -0.42 & 0.46 & 0.04 \\ 545 & 1879 & -0.63 & 0.63 & 1.26 \\ 608 & 1953 & 1.42 & 0.71 & 2.13 \\ 680 & 2028 & 2.55 & 0.84 & 3.39 \\ 730 & 2083 & 3.51 & 1.04 & 4.55 \\ \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

 TABLE III

 Energy Balance at the Surface for Polyethylene

standard air $Y_{0\infty} = 0.232$. To evaluate the mean beam length [eq. (12)], we assumed a conical flame of height $H_c = 5 \times 10^{-3}$ m.

Figure 3 shows the evolution with temperature of radiative flux leaving the flame for the different values of K. The so-calculated values of apparent heat of combustion are respectively 2.70×10^7 J·kg⁻¹ for polyethylene, 2.70×10^7 J·kg⁻¹ for polypropylene, and 2.10×10^7 J·kg⁻¹ for polystyrene.

Evolution of Radiative and Convective Fluxes

When the temperature of the reactor increases, the radiative exchanges with samples are modified for two reasons: the radiative exchange wall-sample varies with the wall temperature; the radiative flux leaving the flame increases with its temperature.

The radiative exchange wall sample (eq. (11)) may be calculated for all reactor temperatures T_{∞} according to the curve T_w vs. T_{∞} (Fig. 2).

In order to determine the radiative flux leaving the flame, it is nessary to know its temperature. But it is not possible to obtain an experimental value of this temperature because the radiative losses suffered by the thermocouple affect very significatively the measured value when temperature increases. We then

	Energy Balance at the Surface for Polypropylene							
			$q_{r_w} =$			$\Delta m \cdot \Delta H_{g}$	/	E
$\underline{T_{\infty}}$	T_w	T_{f}	$\sigma\epsilon_s(T_w^4-T_s^4)$	q_{r_f}	$q_{r_w} + q_{r_f}$	$2\pi R^2$	q_c	defined by
	(°C)			·10 ⁻⁴ (V	W•m ^{−2})			eq. (9)
25	25	1300	-1.59	0.17	-1.42	1.46	2.88	-0.97
100	100	1393	-1.55	0.21	-1.34	1.92	3.26	-0.69
200	205	1481	-1.38	0.29	-1.09	1.55	2.64	-0.70
300	317	1607	-1.00	0.38	-0.62	1.71	2.33	-0.37
400	428	1746	-0.42	0.46	0.04	1.96	1.92	0.02
450	485	1814	-0.04	0.54	0.50	2.34	1.84	0.21
550	608	1961	1.42	0.71	2.13	2.93	0.80	0.73
600	680	2018	2.55	0.84	3.39	3.76	0.37	0.90
650	730	2083	3.51	1.04	4.55	4.68	0.13	0.97

TABLE IV

			Energy Barance ut			styrene		
			$q_{r_w} =$			$\Delta m \cdot \Delta H_{g}$	/	E
T_{∞}	T_w	T_f	$\sigma\epsilon_s(T_w^4-T_s^4)$	q_{r_f}	$q_{r_w} + q_{r_f}$	$2\pi R^2$	q_c	defined by
	(°C)			·10 ⁻⁴ (W•m ^{−2})			eq. (9)
25	25	1150	-1.21	0.33	-0.88	2.17	3.05	-0.40
100	100	1196	-1.13	0.38	-0.75	2.05	2.80	-0.37
300	317	1410	-0.63	0.67	0.04	2.42	2.38	0.02
400	428	1538	-0.17	0.96	0.79	2.72	1.93	0.29
500	545	1683	1.04	1.17	2.21	2.93	0.72	0.76
600	680	1800	2.93	1.55	4.48	4.68	0.20	0.95
650	730	1854	3.89	1.67	5.56	5.64	0.08	0.98

TABLE V Energy Balance at the Surface for Polystyrene

proceeded, by a step-by-step iteration, the determination of the value of E and T_f being given, respectively, by eqs. (9) and (10), from the known values of E and T_f at ambient temperature.

It is then possible to obtain the values of convective fluxes (14):

$$q_c = \frac{\Delta m \cdot \Delta H_g}{2\pi R^2} - (q_{r_w} + q_{r_f})$$

The results are given in Tables III, IV, and V and in Figure 4 for the case of polyethylene.

ANALYSIS OF RESULTS

Apparent Heat of Combustion

The heat of combustion corresponds to the amount of heat released per unit mass of combustible reaching the flame. This value can be theoretically calculated using bond energy calculations if the chemical structure of the polymer and the products of combustion are known.



Fig. 4. Energy balance at the surface in function of the reactor temperature. Case of polyethylene: (•) convective heat flux to the surface; (Δ) Radiative heat flux to the surface $(q_{r_w} + q_{r_f})$; (O) total heat flux to the surface.

The values of ΔH_c for the polymer tested are calculated with tabulated bond energies from Penner,¹¹ in the case of carbon dioxide production.

These values are listed in Table VI along with values found by previous investigators and our experimental values.

There are small differences among the calculated values, especially for polystyrene. This can be due to a discrepancy in the thermodynamic values and in the assumed structure of the gaseous polymer (monomer, more or less large fragments \cdots). The more complicated the structure of the polymer, the less significant is the effect of inclusion or exclusion of one chemical bond. So in the case of polystyrene, it seems that the higher value reported by Blazowski¹² could be explained by the fact that the resonance energy of the benzene cycle is not accounted for.

The comparison of our theoretical and experimental values allows to determine the coefficient γ . These values are, respectively, 0.38 for polyethylene, 0.38 for polypropylene, and 0.48 for polystyrene.

They are higher than those proposed by Kanury¹⁴ (0.21 for polyethylene and polypropylene) and De Ris⁹ (0.13 for polypropylene and 0.43 for polystyrene) concerning larger-scale sample burning in quiescent air.

The higher value of the γ coefficient is observed for polystyrene whose decomposition products are more difficult to oxidize and whose combustion provides soots and smokes. Moreover, the emissivity of the polystyrene flame is higher than that of the two other materials.

The experimental values of heat of combustion conform with the order usually observed for the three studied materials while being weaker. This discrepancy could be attributed to the fact that our tests occur at a lower scale, in an enclosure, and so in confined atmosphere. This configuration could emphasize the incompleteness of the reaction.

The evolution of surface heat fluxes with the reactor temperature (Fig. 4) shows that a blocking effect of the convective flux appears rapidly. Indeed, the raising of the reactor temperature induces an increase of the radiation flux, which leads to an enhancement of the burning rate and so of the mass flux in an opposite direction to the convective one.

In our experimental configuration, the convective flux becomes negligible in the range 600–650°C. Beyond this temperature, the whole heat required by the gasification of the material would be provided by radiation.

The respective behavior of the three studied materials are similar to those observed for large scale fires: polystyrene burns faster with an important release of soots and smokes; its flame is less hot but more luminous and radiative. Polyethylene and polypropylene have very similar behaviors, their burning rates are weaker, and their flames are not very luminous.

TABLE VI	
Heats of Combustion	ì

		$M_c \cdot 10^{-1} (J \cdot kg^{-1}) (c$	calcd values)		Exptl values
	Our values	Blazowski ¹²	Hilado ¹³	De Ris ⁹	ΔH_c^*
Polyethylene	4.37	4.20	4.66	_	2.70
Polypropylene	4.36	4.20	4.66	4.34	2.70
Polystyrene	4.01	4.29	4.15	3.98	2.10

NOMENCLATURE

В	mass transfer driving force
C_p	specific heat capacity $(J \cdot kg^{-1} \cdot K^{-1})$
D	diffusion coefficient $(m^2 \cdot s^{-1})$
E	radiant fraction of feedback
ΔH_c	theoretical heat of combustion (J·kg ⁻¹)
ΔH_g	overall latent heat of degradation (J-kg ⁻¹)
H	flame height (conical) (m)
$h \approx H/R$	nondimensional height of the conical flame
h_c	convective heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$)
i	fuel/oxygen stoichiometric mass ratio (kg _F /kg _O)
k	thermal conductivity $(W \cdot m^{-1} \cdot K^{-1})$
Κ	absorption-emission coefficient (m^{-1})
L	mean beam length (m)
Δm	mass loss of the sample per unit time (kg·s ⁻¹)
m_s	mass flux $(kg \cdot m^{-2} \cdot s^{-1})$
q_{c}	convective heat flux to the surface $(W \cdot m^{-2})$
q_r	radiative heat flux to the surface $(W \cdot m^{-2})$
Q	volumetric heat source sink (W·m ⁻³)
r	coordinate normal to the material surface (m)
R	radius of sample (m)
Т	temperature (K)
W_i	volumetric species source sink (kg of $i \cdot m^{-3} \cdot s^{-1}$)
Yi	mass fraction of species <i>i</i>

Greek

γ	ratio of the total heat lost by flame to the theoretical heat produced by combustion
E	emissivity
ρ	density (kg·m ⁻³)

σ	Stefan–Boltzmann	constant (J•m ⁻² •K ⁻⁴)
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Subscripts

f	flame
F	fuel
g	gas
i	species
0	oxygen
\$	material surface
w	reactor wall
80	ambience

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