Combustion of polystyrene spheres in air

Basavanahalli N. Raghunandan and Hanasoge S. Mukunda

Department of Aeronautical Engineering, Indian Institute of Science, Bangalore 560012, India

Mass histories of polystyrene spheres (initial diameter 2—5 mm) burning in simulated air have been obtained by quenching combustion after variable times and weighing the residues. The flame positions and temperature histories of the spheres have also been recorded. A simple analytical model — an extension of quasi-steady combustion theory of liquid droplets — is shown to describe the combustion process reasonably well. Though the combustion process is broadly similar to that of liquid spheres, flame diameter is relatively smaller, particle temperature higher, and decomposition reactions occur in the condensed phase.

Study of combustion of polymers has applications in several fields, including those of aerospace and fire hazards. In the present paper some basic characteristics of combustion of polymers are elucidated using the technique of polymer-sphere combustion in an oxidizing atmosphere. Combustion of polymers has been studied in many geometries, e.g. flat-plate boundary layer[1], wall-jet diffusion flame[2], strand combustion[3], and combustion of spheres[4-6]. The last has certain advantages, namely well defined geometry, existence of a bounded analytical solution in gas phase (in a spherically symmetrical case), availability of a large amount of experimental data on liquid-sphere combustion which is of the same nature, and simplicity of experimental technique.

The similarity between the combustion processes of liquid droplets and polymer spheres has been well recognized[4]. Any difference in the combustion characteristics of the two must arise from structural differences in the condensed phase. In the following Sections, we discuss how the experimental data can be obtained and what factors need be considered to extend the simple quasi-steady theory of droplet combustion[7] to polymer-sphere combustion.

EXPERIMENTAL

Technique

The simplest of the sphere-combustion techniques and the one that can be directly used for polymer spheres is the burning of stationary spheres in quiescent air. A few preliminary experiments revealed that the polymer spheres swell after ignition for a few seconds and that the equivalent diameter changes little in the period during which data can be recorded. Such trials, made using a cine camera, implied that one should actually measure the mass loss by some means other than the diameter reduction to assess the combustion characteristics. This also eliminates the ambiguity involved in defining an equivalent diameter. However, photography is indispensable if the flame position is to be recorded.

A continuous mass-loss measuring system would definitely be a sound technique for burning-rate determination, but the technical difficulties seemed to be such that this technique has not been used here. The problems with such a

technique are: (i) Natural convection. The buoyancy forces on the burning polymer sphere are of unknown magnitude, are time-varying, and can be of the same order as mass loss itself. An attempt was made to balance this force by having a heated metallic sphere on the other arm of the balance as in ref. 6. But simulation of identical condition on either side would be difficult owing to the elongated flame on the polymer sphere, whose size itself may change, and the lower drag coefficient of burning spheres compared with that for a solid sphere with no mass exchange (see ref. 8). (ii) Transient effects created during ignition. Polymer spheres, especially larger ones, require a pilot flame for ignition. Such a process of ignition was found to produce fairly large oscillations in the balance. Though the combustion of polymer spheres comes to a normal state (i.e. with the full envelope flame having been formed) the oscillations of the arm of the balance continue for a longer period. This can possibly be eliminated by providing large viscous damping pots in the balance, but then the response of the balance to weight-loss rate will decrease.

Hence, the technique adopted here is to measure the weight of the sphere intermittently after quenching. Shyu *et al.*[9] have used this technique to obtain mass histories of multicomponent heavy fuel drops during combustion and evaporation. But in the case of polymers, ignition times being long, with every ignition (similarly quenching) some amount of cumulative inaccuracies is introduced. Therefore, it is necessary to burn many identical spheres and quench at different times in order to obtain a mass *vs.* time plot. Since identical spheres are required, one has to resort to a moulding technique. In the present work, injection moulding has been used to get spheres of four different sizes (2 mm, 3 mm, 4 mm and 5 mm dia.) from a commercial polymer 'General Purpose Polystyrene (GPP)'. It has been determined that the heat of combustion of GPP is 37.7 kJ/g, and its heat of vaporization (including degradation) appears to be larger than that of pure polystyrene as determined from DTA traces.

Apparatus and procedure

Figure 1 is the schematic drawing of the experimental set-up. It consists of a cylindrical glass combustion chamber
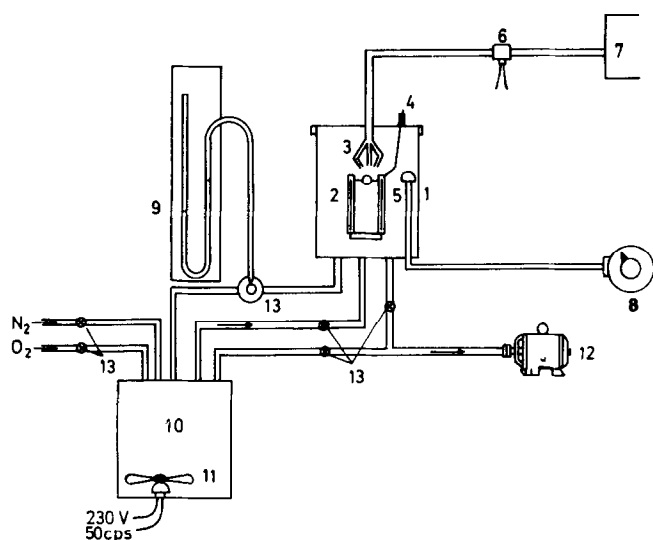
Figure 1 Schematic view of the experimental set-up

1 Combustion chamber
2 Polymer sphere on the support
3 Quenching jets
4 Rotating arm
5 Coil for pilot ignition
6 Solenoid valve
7 Low-pressure N_2/air source
8 High-amperage auto-transformer
9 Manometer
10 Mixing chamber
11 Fan for mixing
12 Vacuum pump
13 Valves

of diameter 14·8 cm and height 20 cm. The top cover has a rotating arm which is used for ignition along with a small heating coil inside the chamber. A matchstick or a slow-burning propellant strand is attached to the lower end of the arm and is rotated in assembly so that it first touches the coil to become ignited and then comes directly under the polymer sphere, supported on a horizontal quartz fibre. It can be quenched by making it touch the cold wall of the chamber after ignition of the polymer has been effected. The quenching system consists of claw-like tubes inside the chamber which have connection to a low-pressure-nitrogen source through a solenoid valve. The latter arrangement is used for instantaneous quenching of the burning sphere at any desired time. The mixing chamber, vacuum pump and mercury manometer are all connected to the combustion chamber so that any part can be isolated and held at the required pressure level, and to vary the ambient composition. The experimental data reported below, however, refer to polystyrene spheres burning in simulated air.

Photographs are taken with an intense back-light using a cine camera at 16 frames/s. The pictures obtained help in identifying the instants of ignition and quenching fairly accurately. Also the flame position and sphere surface can be well identified. The photographic system has been checked to ensure that the curvature of the wall does not produce any significant distortion. The mass measurement has been made using a chemical balance accurate to 0·1 mg. The measurements of flame and sphere diameters from the pictures are made with a travelling microscope to an accuracy of 0·01 mm.

The temperature histories of the cores of the burning spheres have been traced by using a Pt—Pt/Rh thermocouple in place of quartz fibre. These experiments are conducted in open air.

In the experiments conducted, a small amount of leakage was provided in order to avert the depletion of oxygen concentration in the surrounding medium. It has been estimated that such leakage results in a flow with Reynolds number of

about 2—3, which is very small. (See ref. 10 for more details.) It can safely be concluded that the combustion of GPP spheres takes place in the presence of natural convection, forced convection being nearly absent.

Experimental data

Physical observations and observations of 16 mm cine photographs showed that after a period of 4—5 s the flame gets locally distorted owing to sputtering of the fuel at certain locations. Some quenched samples when cut into two halves and examined revealed the formation of gas pockets after 4—5 s. Sputtering is hence thought to be the beginning of the formation of gas pockets. *Figure 2* shows a schematic representation of the polymer sphere with the flame, the various dimensions being inscribed on it. *Table 1* shows the average ignition time and the ratio of flame to sphere diameter, using the notation shown in *Figure 2*. These measurements were the average of at least five experiments. The deviation from this mean value rarely exceeded 5%. It may be observed that the flame-to-sphere ratio is small compared with that of liquid spheres under similar conditions ($\approx 3 \cdot 0$).

Figure 3 shows the raw data obtained from the experiments on GPP spheres burning in air. A careful observation of the data points seems to suggest the possibility of an increasing burning rate with time. A representative burning rate can however be obtained by the slopes of approximated straight lines as shown in the Figure (insert). The equivalent burning constant obtained, K, seems to be slightly lower than that for liquid hydrocarbon droplets.

The core temperatures *vs.* time as recorded are shown in *Figure 4*. The first plateau-like region is due to the withdrawal of the ignition source at the instant when the diffusion flame of the GPP sphere is seen to have formed. At the range marked 'G', there is a sudden increase in the gradient. This is the instant when the sphere melts and drops allowing the thermocouple bead to enter the gas phase. It is a good approximation to take this point as the surface temperature ($\approx 740 \pm 30$ K). The temperature traces obtained by Waibel and Essenhigh[5] show a similar trend, but they have not quoted the temperature values. The value obtained for the surface temperature in the present experi-
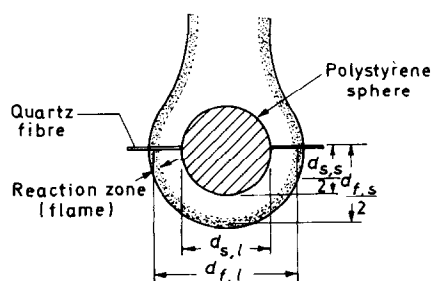

Figure 2 Diagram showing a sphere and typical flame

Table 1 Ignition time and (d_f/d_s) for GPP spheres

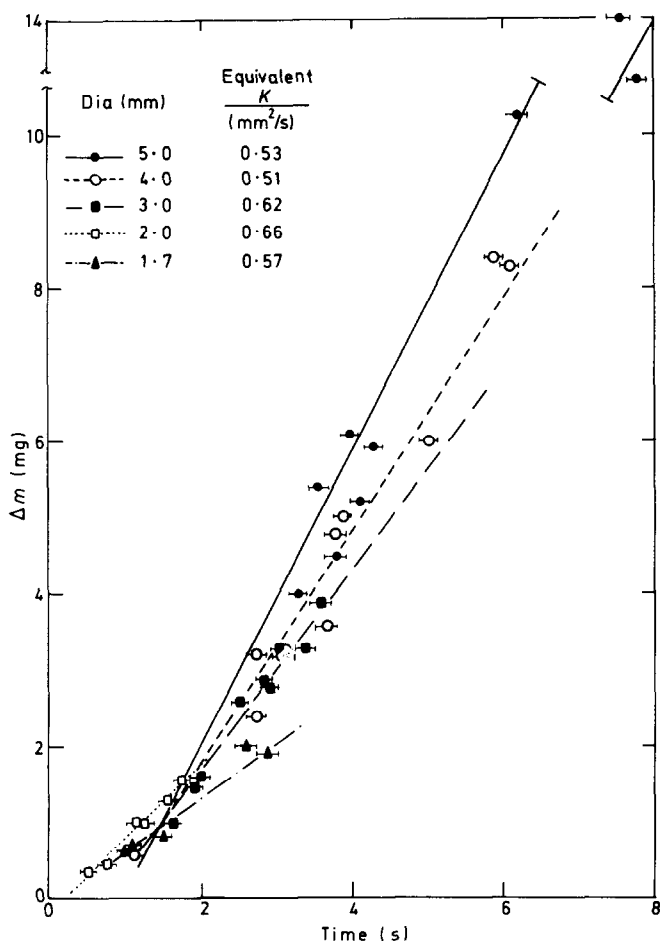| Diameter (mm)	Average ignition time (s)	d_f/d_s at stagnation point $(d_{f,s}/d_{s,s})$	at lateral position $(d_{f,l}/d_{s,l})$
5·0	4·22	1·38	1·51
4·0	3·37	1·47	1·49
3·0	2·49	1·61	1·63
2·0	1·67	1·67	1·97

Figure 3 Experimental data of mass loss *vs.* time for GPP spheres burning in air

ment is about the same as that quoted in ref. 4 for polystyrene.

The above results are further discussed in the following Section in the light of a theoretical model.

THEORETICAL

The model

The combustion of polymer spheres differs from that of liquid droplets mainly in terms of the condensed phase and interfacial processes. A polymer has to degrade from a long chain to small fragments before becoming vapour. This involves additional heat transfer into the condensed phase. The core and surface temperatures being high, the sensible enthalpy term also is larger for polymer spheres. The process of heating up of the sphere introduces an unsteadiness in the heat transfer.

Further, at the surface, it can be argued that the vaporization follows a rate process. If equilibrium is to prevail at the surface then there is a definite relation between the surface temperature, the partial pressure of the vapour in the adjacent gas phase and the molecular weight of the fuel vapour. From the boiling points of a series of alkanes as a function of molecular weight it turns out that if the surface temperature is around 700—800 K (experimentally measured range), then the corresponding vapour molecular weight will be more than, say, 1500. But it is known that the average molecular weight of polystyrene vapours at 600 K is around 200—300 [11]. Even after allowing for changes due to higher temperature, it is unlikely that such large mole-

cules as the former can exist in the gas phase. It therefore appears from this feasibility argument that the rate law is a more appropriate description for the surface processes of the polymer.

Analysis

The following mathematical model is along the same lines as that of Waibel and Essenhigh [5], with appropriate modifications taking into account the above-mentioned features of polymer-sphere combustion.

The rate of rise of sensible enthalpy, $\dot{Q}$, of the droplet is written in the form

$$\dot{Q} = mC_c \frac{dT_s}{dt} \qquad (1)$$

where m is the mass of the sphere and C_c is the specific heat of the polymer, assuming that the whole sphere is at a temperature T_s.

The effective heat of vaporization q_p includes two terms, the heat of vaporization, Δh_{vap} and the heat of degradation, Δh_{deg}:

$$q_p = \Delta h_{vap} + \Delta h_{deg} \qquad (2)$$

Reference 5 does not seem to include the degradation term, which is one of the primary factors distinguishing the polymer from liquid droplets.
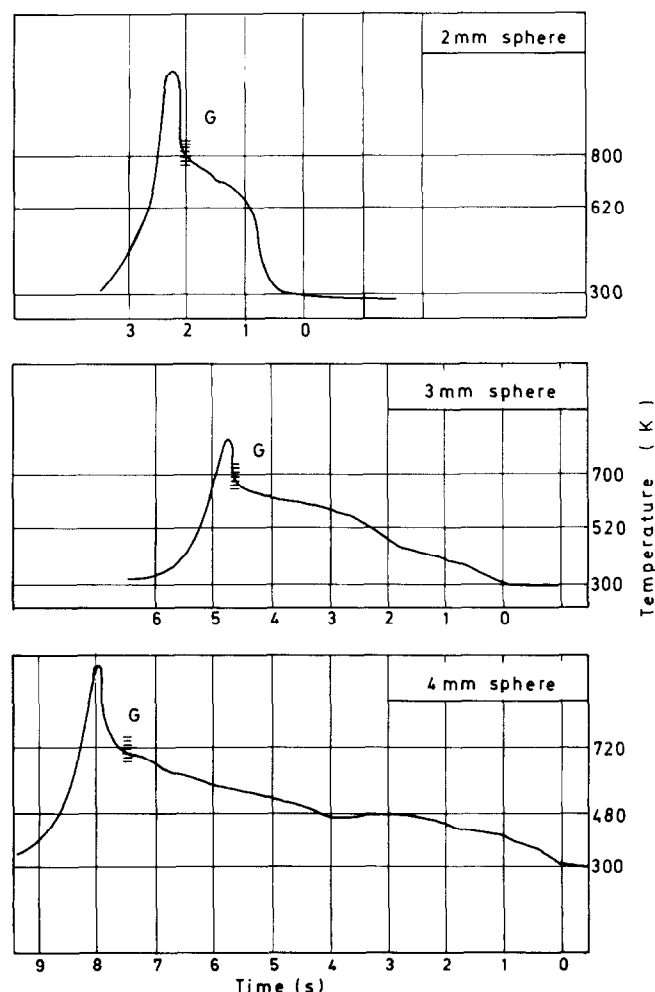

Figure 4 Core temperature *vs.* time for GPP spheres

The surface condition for the burning sphere can be written in the form

$$\dot{r} = Ae^{-E_s/RT_s} \tag{3}$$

where $\dot{r}$ is the linear regression rate, A the preexponential factor, E_s the activation energy, and R the universal gas constant.

So, the heat transfer boundary condition can now be written as:

$$4\pi r_s^2 \lambda \frac{dT}{dr}\bigg|_+ = \dot{m}\left(q_p + \frac{\dot{Q}}{\dot{m}}\right) \tag{4}$$

λ being the thermal conductivity in the gas phase.

Compare this with the condition used for liquid droplets in the simple quasi-steady theory (SQST), namely

$$4\pi r_s^2 \lambda \frac{dT}{dr}\bigg|_+ = \dot{m}L \tag{5}$$

where L is the latent heat of vaporization of the liquid, and which finally gives the mass burning rate $\dot{m}$ as[7]:

$$\dot{m} = 4\pi\frac{\lambda}{c_p}r_s \ln\left(1 + \frac{c_p(T_\infty - T_s) + H\beta/s}{L}\right) \tag{6}$$

We can write, for a polymer sphere:

$$\dot{m} = 4\pi\frac{\lambda}{c_p}r_s \ln\left(1 + \frac{c_p(T_\infty - T_s) + H\beta/s}{q_p + \dot{Q}/\dot{m}}\right) \tag{7}$$

where c_p is the constant pressure specific heat in the gas phase, T_∞ and β are the ambient temperature and oxidizer concentration respectively, H is the heat of combustion of the material of the sphere, and s is the stoichiometric ratio for the combustion process.

Combining equations (1) and (7), we write:

$$\frac{dT_s}{dt} = \frac{\dot{m}}{mC_c}\left[\frac{c_p(T_\infty - T_s) + H\beta/s}{\xi - 1} - q_p\right] \tag{8}$$

where

$$\xi = \exp\left[\frac{\dot{m}c_p}{4\pi r_s\lambda}\right]$$

It may be mentioned here that equation (8) is the corrected form of the equation in ref. 5 which is in error.

For a polymer sphere of given size burning in an oxidizing atmosphere, $\dot{m}$, T_s and other parameters can be evaluated as functions of time using equations (3), (4), (7) and (8). The specification of initial state is made through the condition that the flame starts from the surface at $t = 0$, i.e.

$$\dot{m}(t = 0) = 4\pi\frac{\lambda}{c_p}r_s\ln(1 + \beta/s) \tag{9}$$

Equations (9) and (3) together provide T_s ($t = 0$).

The ratio of flame diameter (d_f) to drop diameter (d_s) at any time is written as:

$$\frac{d_f}{d_s} = \frac{\ln\left[1 + \dfrac{c_p(T_\infty - T_s) + H\beta/s}{q_p + \dot{Q}/\dot{m}}\right]}{\ln[1 + \beta/s]} \tag{10}$$

Numerical scheme

In order to evaluate the mass-loss with time, which can be compared with the experimental data on GPP spheres, equation (3) has been written in the form:

$$\dot{m} = 4\pi r_s^2\rho_c A\exp(-E_s/RT_s) \tag{11}$$

so that the observed constant-radius and variation in density (ρ_c) are taken into account. The scheme of computation, in brief, is as follows:

(i)   The radius of the sphere at $t = 0$ and all the thermodynamic, transport and kinetic constants are specified (see *Table 2*)

(ii)   Equations (9) and (11) give T_s ($t = 0$).

(iii) Again equations (11) and (8) give $\dot{m}$ and dT_s/dt; d_f/d_s is obtained from equation (10).

(iv)   Using a suitable time step (such that any further reduction in time step does not significantly affect the overall results) the values of T_s and $\dot{m}$ at the next time step are evaluated.

The steps (iii) and (iv) are repeated till the time of burning roughly corresponds to the experimentally recorded time during which no core-formation takes place.

Results and discussion

The choice of activation energy and pre-exponential factor plays a significant role in the theoretical estimation of mass-loss rate. From the number of values for E quoted in the literature a meaningful selection of E has to be made.

The mass-loss *vs.* time curves for a 5 mm sphere with various kinetic constants are shown in *Figure 5*. It is clear that the value of E (= 50.2 kJ/mol) taken from ref. 12 appears to produce a good matching between the theoretical curve and the experimental data. It may be noted that the

Table 2   Properties used in calculations for polystyrene—air system

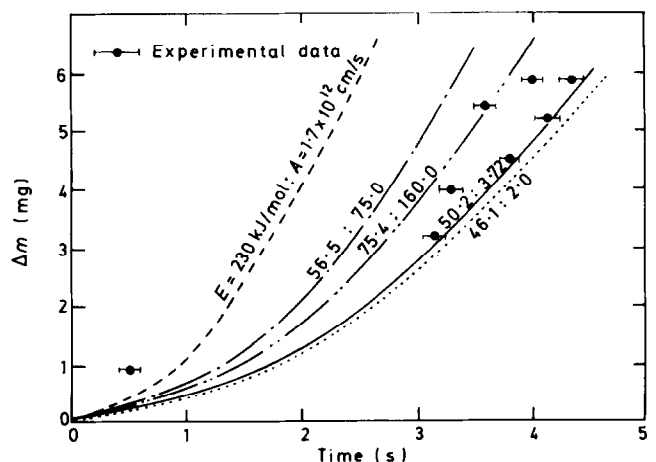|	
C_c = 1·34 J/g °C	Δh_{vap} = 419 J/g (ref. 12)
C_p = 1·26 J/g °C	Δh_{deg} = 670 J/g (ref. 12)
H = 37·7 kJ/g fuel	ρ_c (at t = 0) = 1·06 g/cm^3
β = 0·232	λ = 1·26 mJ/cm s K = 0·126 W/m K
S = 3·077	T_∞ = 300 K

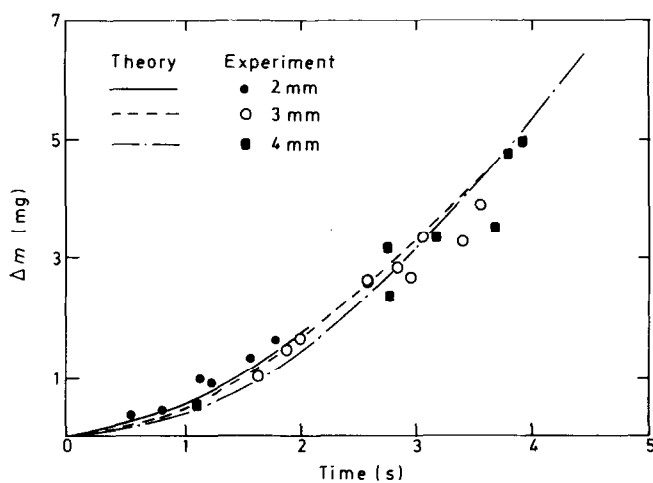Figure 5   Effect of E on mass loss *vs.* time for 5 mm GPP sphere

Figure 6 Mass loss *vs.* time for GPP spheres: comparison of theory with experimental data (E = 50·2 kJ/mol, A = 3·72 cm/s)
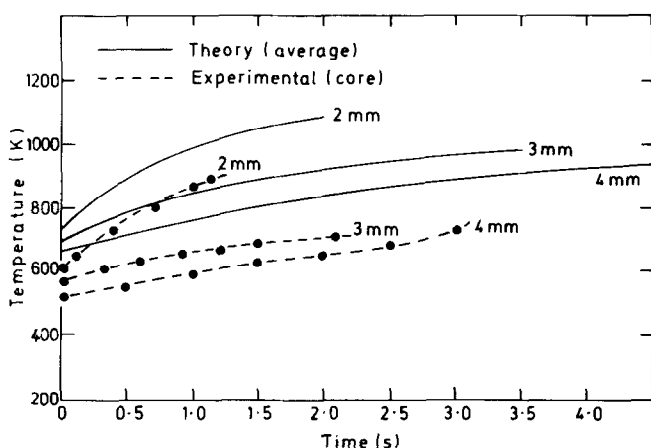

Figure 7 Comparison of theoretical and experimental temperature histories
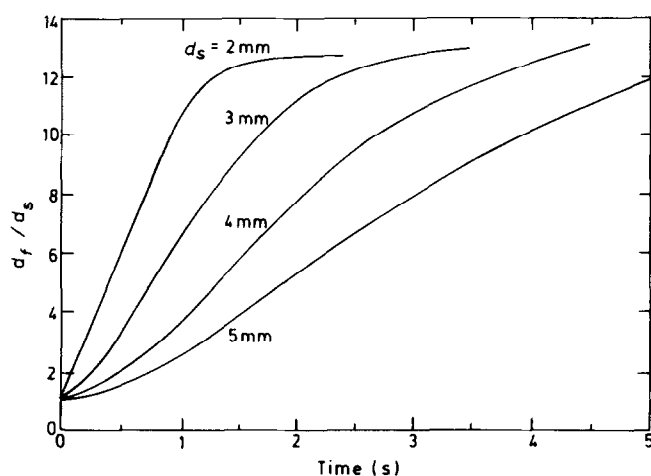

Figure 8 Theoretical prediction of variation of d_f/d_s with time for polymer spheres

spheres. These results are seen in *Figure 6*. Once again, reasonable matching is observed.

Figure 7 shows the trends of T_s vs. time from ignition onwards of the spheres. Also shown in the Figure are the experimental data. It must be noted that the experimental data refer to the temperature at the centre of the sphere, and the theoretical T_s to an average temperature for the whole sphere. As such the higher value of the latter is easily understandable. In view of the approximate nature of the theory, the similarities between the theoretical and experimental curves appear satisfactory. The higher values of T_s for smaller spheres are consequences of the equations (7) and (11) leading to $1/r_s \approx \exp(-E/RT_s)$. The final constant value of T_s would correspond to the quasi-steady prediction with $dT_s/dt = 0$.

The variation of the ratio d_f/d_s with time for different sizes of GPP spheres is shown in *Figure 8*. Because the term q_p includes the heat of degradation also, the final values of d_f/d_s predicted by SQST are very small compared to those for liquid droplets (≈ 30). The effect appears only through the transfer number B, which is low for polymers owing to high T_s and q_p. As the term $dT_s/dt \to 0$, d_f/d_s becomes independent of the diameter of the sphere, and a steady state sets in. However, the absolute values of d_f/d_s are much higher than the experimental values. Apart from the fact that natural convection under experimental conditions has reduced d_f/d_s considerably, there is an inherent defect in the SQST. As mentioned earlier, even for liquid droplets the SQST overestimates the d_f/d_s almost three times. The reasons for this discrepancy have been well diagnozed in ref. 10. A detailed variable-property analysis in the gas phase should predict the values more accurately.

CONCLUSIONS

The experimental and theoretical studies presented in this paper have shown that:

1. The mass-loss measurement, not the diameter measurement, is the correct technique for estimating the burning rate of polymer spheres. A method has been set out to obtain the data.

2. The burning of a polymer sphere, though it appears very much like a liquid droplet combustion, differs from the latter considerably in that the ratio d_f/d_s is smaller and the condensed-phase temperature is very high. The gaseous-core formation indicates the reactive processes taking place inside the sphere. Thus the condensed-phase structure seems to be important.

3. With an approximate analysis, accounting for the condensed-phase temperature rise and the heat of degradation, the mass loss vs. time for burning polymer spheres can be reasonably predicted. The choice of activation energy and pre-exponential factor from the literature made in this connection is consistent with experimental data of four different sizes of GPP.

experimental conditions in ref. 12 do correspond to the present ones, the similarities being (a) laminar diffusion flame, (b) absence of oxidative attack, (c) material being commercial polystyrene (as in our GPP), and (d) rectilinear pyrolysis data (as is the assumed boundary condition, equation (3)).

The choice of kinetic constants is further checked against the experimental data on 2, 3 and 4 mm diameter GPP

REFERENCES

1   Kumar, R. N. and Stickler, D. B. *Thirteenth Symposium (International) on Combustion,* The Combustion Institute, Pittsburgh, 1971, p 1059
2   Blazowski, W. S., Cole, R. B. and McAlevy, R. F. III. *Tech. Rep. M.E.-RT 6004,* Stevens Inst. Tech., Hoboken, N. J., 1971
3   Martin, F. J. *Combust. Flame* 1968, 12, 127

4   Essenhigh, R. H. and Dreier, W. L. *Fuel* 1969, 48, 330
5   Waibel, R. T. and Essenhigh, R. H. *Fourteenth Symposium (Int.) on Combustion,* The Combustion Institute, Pittsburgh, 1973, p 1413
6   Kuwata, M., Stumbar, J. P. and Essenhigh, R. H. *Twelfth Symposium (Int.) on Combustion,* The Combustion Institute, Pittsburgh, 1969, p 663
7   Godsave, G. A. E. *Fourth Symposium (Int.) on Combustion,* Williams and Wilkins, Baltimore, 1953, p 818
8   Eisenklam, P., Arunachalam, S. A. and Weston, J. A. *Eleventh Symposium (Int.) on Combustion,* The Combustion Institute, Pittsburgh, 1967, p 715

9   Shyu, C. R., Chen. C. S., Goudie, G. O. and El-Wakil, M. M. *Fuel,* 1972, 51, 135
10   Raghunandan, B. N. *PhD Thesis: Diagnostic Studies on the Combustion of Liquid and Polymer Spheres,* Indian Institute of Science, Bangalore, 1976
11   Madorsky, S. L. *Thermal Degradation of Organic Polymers,* Interscience Publishers, John Wiley and Sons Inc., New York, 1964
12   Hansel, J. G. and McAlevy, R. F. III., 'Energetics and Chemical Kinetics of Polystyrene Degradation in Inert and Chemically Reactive Environments', *Paper 65–58, AIAA 2nd Aerospace Sciences Meeting,* New York, 1965