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Heterogeneous Combustion Studies on Polystyrene and Oxygen Styrene Copolymer

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The hybrid combustion of polystyrene and oxygen styrene copolymer has been studied. The linear regression rate r and total mass flow of fuel m_f have been measured at different oxygen flow rates and at different times intervals. It is found that the regression rate decreases with time. Detailed analysis of the data shows that it is due to radiative heat transfer from the flame zone to exhaust gases.

Nomenclature

A = initial radius, cm
a = constant, cm^4/g
B = blowing parameter, mass transfer number $\Delta h_T/\Delta H$
C_f = skin-friction coefficient in presence of blowing
C_{f_o} = skin-friction coefficient in absence of blowing
C_H = Stanton number
D = instantaneous duct diameter, cm
D_o = initial duct diameter, cm
G_o = oxidizer mass flux, g/cm^2 sec
G = total specific mass flow rate, g/cm^2 sec
Δh_T = sensible enthalpy difference between the flame and wall, cal/g
ΔH = heat of gasification, cal/g
K = const
K_i = const; $0.6\,(G_o L/\mu)^{-0.2}$
L = length of the grain, cm
n = empirical constant
m_f = total mass flow of fuel, g/sec
m_{ox} = total mass flow of oxidizer, g/sec
Pr = Prandtl number of gas mixture
$\dot{Q}_w$ = total heat transfer
$\dot{Q}_c$ = convective heat transfer
$\dot{Q}_r$ = radiative heat transfer from the flame front to the wall
$\dot{Q}_{re}$ = radiative heat transfer from the flame front to the exhaust gases
r = radius of the grain
r = regression rate cm/sec
$\bar{r}$ = average regression rate, cm/sec
Re_x = Reynolds number $(G_o x/\mu)$
t = time, sec
T_r = flame temperature
u_∞ = freestream velocity
x = distance from the surface
z = optical path length, diameter of the grain, cm
α = empirical radiation coefficient
β = empirical pressure exponent
ε_g = emissivity of the fluid
ε_w = emissivity of the surface
μ = viscosity of the oxidizer
ρ_f = density of the fuel
ρ_e = density at edge of boundary layer
σ = Stefan-Boltzmann constant
λ = weight fraction of gas in the decomposed fuel at equilibrium wall temperature.

Subscripts

o = initial, axis or oxidizer
e = boundary-layer edge
f = fuel

Introduction

BALLISTIC behavior of hybrid propellants is a subject of considerable current interest.[1,2] Quite recently Rastogi and Baijal[3] have investigated the hybrid combustion of boron containing polymers. The regression rate was found to decrease with time and it was tentatively suggested to be due to radiative heat transfer to the unreacted oxidizer. The present paper deals with the hybrid combustion in polystyrene/oxygen and in copolymer/oxygen systems where similar results are obtained. However, the present investigation is more thorough and the results have been examined analytically to illustrate convincingly the role of radiative heat transfer.

Theory

In hybrid combustion, gasification of the fuel occurs and flame appears on account of heat release during the reaction between gaseous degradation products and oxidizer. Heat transfer to the surface takes place leading to further gasification and subsequent chemical reaction. In most of the hybrid systems chemical reactions occur very fast and the heat transfer is the rate determining step. The simple heat balance equation can be written[1,4] as follows:

$$r\rho_f \Delta H = \dot{Q}_w \tag{1}$$

where

$$\dot{Q}_w = \dot{Q}_c + \dot{Q}_r - \dot{Q}_{re} \tag{2}$$

We shall consider the case when $\dot{Q}_r$ and $\dot{Q}_{re}$ are negligible compared to $\dot{Q}_c$. The convective heat transfer $\dot{Q}_c$ is given by

$$\dot{Q}_c = C_H \rho_e u_\infty \Delta h_T \tag{3}$$

For gases, it is known that

$$C_H Pr^{2/3} = C_f/2 \tag{4}$$

when hybrid boundary layer is assumed to be turbulent, so that

$$\rho_f \dot{r} = \rho_e u_\infty (C_f/2) \qquad \Delta h_T/\Delta H = \rho_e u_\infty (C_f/2) B \tag{5}$$

since $Pr = 1$. For most of the cases from experimental data[5,6] we have

$$C_f/2 = 0.03 Re_x^{-0.2} \qquad \text{(for turbulent flow)} \tag{6}$$

and

$$C_f/2 = 0.332 Re_x^{-0.5} \qquad \text{(for laminar flow)} \tag{7}$$

On combining Eqs. (5) and (6) we get

$$\rho_f \dot{r} = 0.03 G Re_x^{-0.2} (C_f/C_{f_o}) B \tag{8}$$

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Index categories: Fuels and Propellants, Properties of; Combustion in Heterogeneous Media; Solid and Hybrid Rocket Engines.

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According to Marxman[7] C_f/C_{f_o} is found to be related to B as follows:

$$C_f/C_{f_o} = 1.2B^{-0.77} \tag{9}$$

Substituting the value of C_f/C_{f_o} from Eq. (9) in Eq. (8), we get

$$\rho_f \dot{r} = 0.036G \cdot Re_x^{-0.2} B^{0.23} \tag{10}$$

Since Re_x is equal to $G(x/\mu)$, we get

$$\rho_f r = 0.036(x/\mu)^{-0.2} G^{0.8} B^{0.23} \tag{11}$$

Equation (11) can be put in the following form

$$r = aG^{0.8} \tag{12}$$

where

$$a = 0.036/\rho_f (x/\mu)^{0.2} B^{0.23} \tag{13}$$

Radiative Heat Transfer

In the preceding discussion, we have only taken into account the convective heat transfer. However, heat transfer from the flame zone to the wall and to the exhaust gases by radiation would also be important. As a first approximation, we may neglect $\dot{Q}_r$. Accordingly, we write

$$r \rho_f \Delta H = \dot{Q}_c - \dot{Q}_{re} \tag{14}$$

so that at a particular instant

$$r = \dot{Q}_c / \rho_f \Delta H - \dot{Q}_{re} / \rho_f \Delta H \tag{15}$$

The radiant heat transfer flux from the combustion products to the exhaust gases would be given by the familiar law,[1]

$$\dot{Q}_{re} = \sigma \varepsilon_w \varepsilon_g T_r^4 \tag{16}$$

The fluid emissivity is given by the relation

$$\varepsilon_g = 1 - e^{-\alpha p z} \tag{17}$$

Thus,

$$\dot{Q}_{re} = \sigma \varepsilon_w p^{*\beta} T_r^4 (1 - e^{-\alpha p z}) \tag{18}$$

Since at $t = 0$

$$\dot{Q}_{re} / \rho_f \Delta H = 0 \tag{19}$$

Equation (15) can be rewritten as

$$r_t = r_o - \dot{Q}_{re} / \rho_f \Delta H \tag{20}$$

It follows from Eq. (20) that r would decrease with time since the factor $\dot{Q}_{re}/\rho_f \Delta H$ increases with time. Using Eqs. (18) and (20) we can write

$$r_t = r_o - (\sigma \varepsilon_w p^{*\beta} T_r^4 / \rho_f \Delta H)(1 - e^{-\alpha p z}) \tag{21}$$

On rearranging Eq. (21) we have

$$[\rho_f \Delta H / \sigma \varepsilon_w p^{*\beta} T_r^4)(r_t - r_o) + 1] = e^{-\alpha p z} \tag{22}$$

or

$$\mathrm{Log}\,[(\rho_f \Delta H / \sigma \varepsilon_w p^{*\beta} T_r^4)(r_t - r_o) + 1] = -\alpha p z \tag{23}$$

Equation (23) can be used to examine the contribution of radiative heat transfer from the flame zone to the exhaust gases. It should be noted that when Eq. (2) is used in place of Eq. (4), time-dependence of burning rate would still be predicted since $\dot{Q}_r$ would be largely time-independent.

Experimental

Preparation of Polymers

Polystyrene and copolymer of oxygen and styrene were prepared in a manner as described earlier.[8]

Regression Rate Studies

A cylindrical grain of polymer of length 6 cm and o.d. 3.5 cm having a hole of diameter 0.6 cm was placed in the hybrid burner. Oxygen gas at 1 atm pressure was allowed to pass through the hole at a definite flow rate. The sample was ignited electrically by a nichrome wire. Whenever needed, the combustion was stopped by sudden quenching with the help of nitrogen gas. The port diameter at the two ends after burning was measured. The mass of the sample burnt was also measured by weighing the sample before and after burning. The measurements were repeated for different burn times, keeping the flow rate of oxygen constant. Similar experiments were repeated at different flow rates. The mass flow rate of fuel $\dot{m}_f$, instantaneous regression

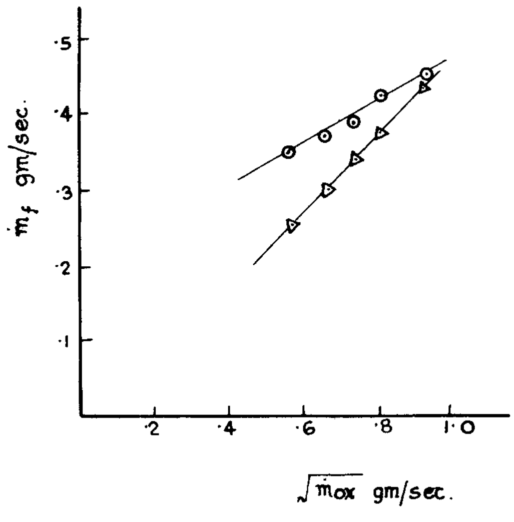

Fig. 1 Dependence of total mass flow of fuel on total mass flow of oxidizer. ○ Copolymer; △ Polystyrene.

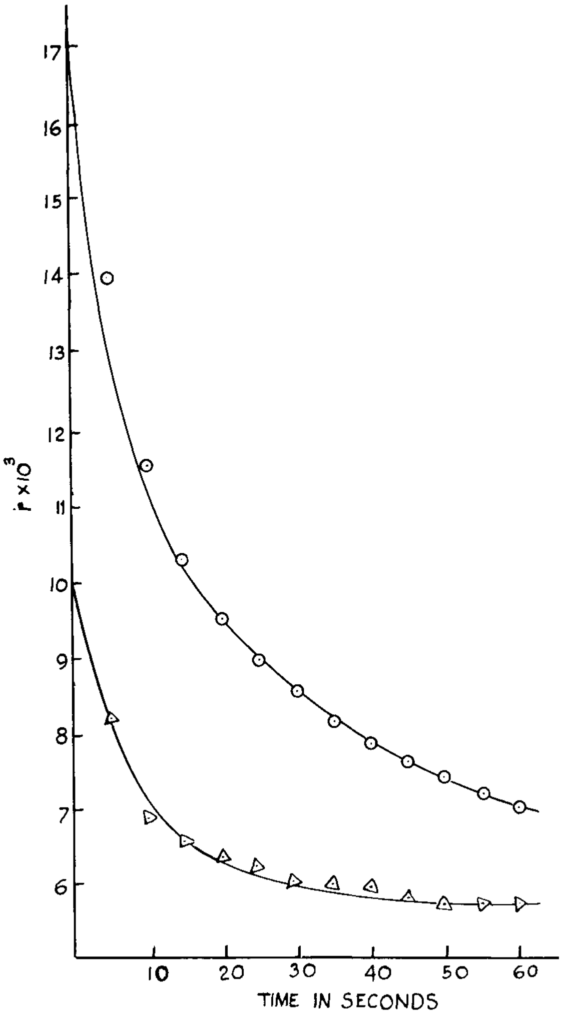

Fig. 2 Variation of regression rate with time. ○ Copolymer; △ Polystyrene.

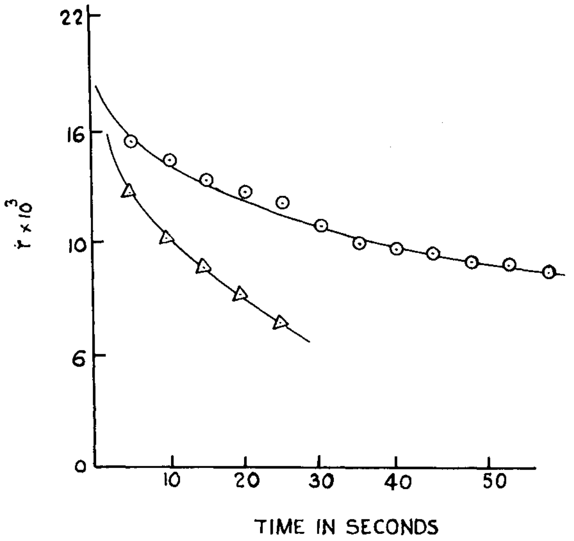

Fig. 3 Comparison of experimental regression rate and the calculated one using Eq. (27) for polystyrene. ⊙ Experimental; △ Calculated.

rate r, and average regression rate $\bar{r}$ were estimated from the abovementioned data for each polymer fuel. The measurements were made at constant pressure (1 atm pressure).

Flame Temperature Measurement

The flame temperature was measured by a sodium line-reversal technique[9] using an iodine-filled tungsten filament lamp as a standard source. The stray light from the flame was minimized by placing a diaphragm between the flame and the direct vision spectroscope. The lamp intensity-temperature calibration was done by using an optical pyrometer. Proper corrections were made for red light shift to yellow sodium-D lines[9] for light filters of pyrometer. During measurements, the hybrid burner was fixed vertically so that the filament image was 1.5 cm above the top of the burner.

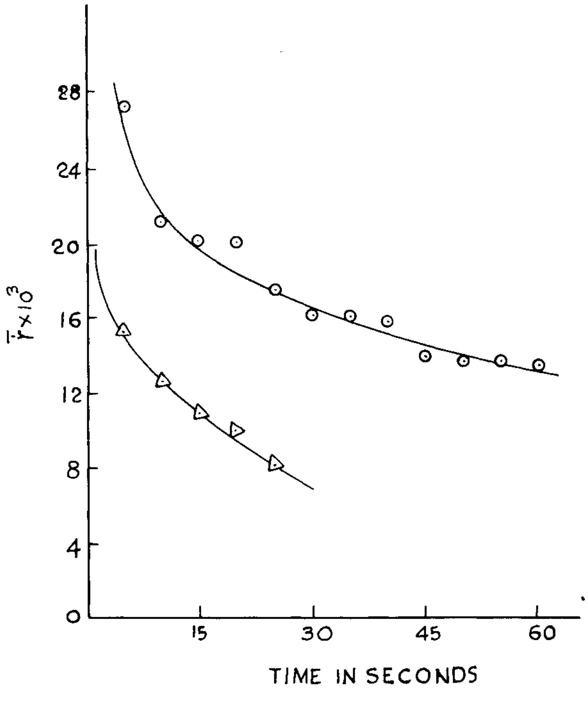

Fig. 4 Comparison of experimental regression rate and the calculated one using Eq. (27) for copolymer. ⊙ Experimental; △ Calculated.

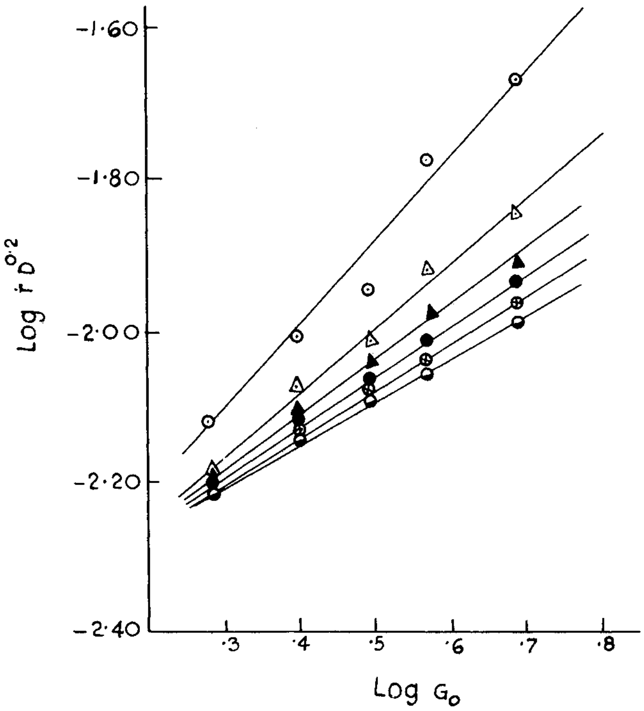

Fig. 5 Dependence of regression rate on the oxidizer flow rate for polystyrene. ⊙ 5 sec; △ 15 sec; ▲ 25 sec; ● 35 sec; ⊗ 45 sec; ◒ 55 sec.

Discussion

Results plotted in Fig. 1 show that m_f is related to m_{ox} by the relation

$$m_f = \text{const}\, m_{ox}^{0.5} \tag{24}$$

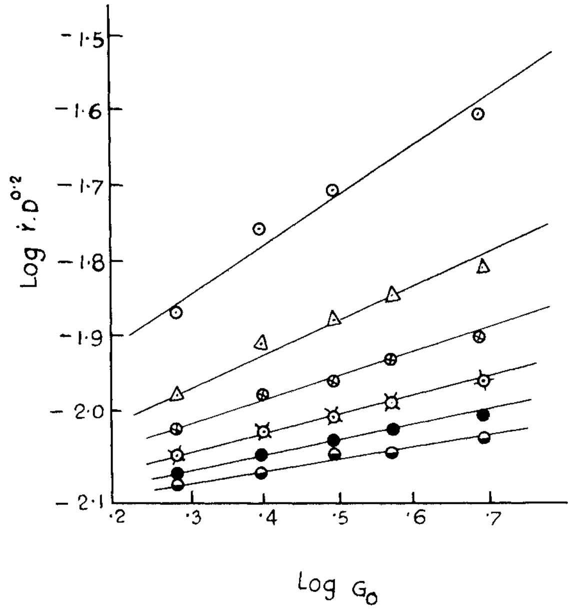

Fig. 6 Dependence of regression rate on the oxidizer flow rate for copolymer. ⊙ 5 sec; △ 15 sec; ⊗ 25 sec; ☼ 35 sec; ● 45 sec; ◒ 55 sec.

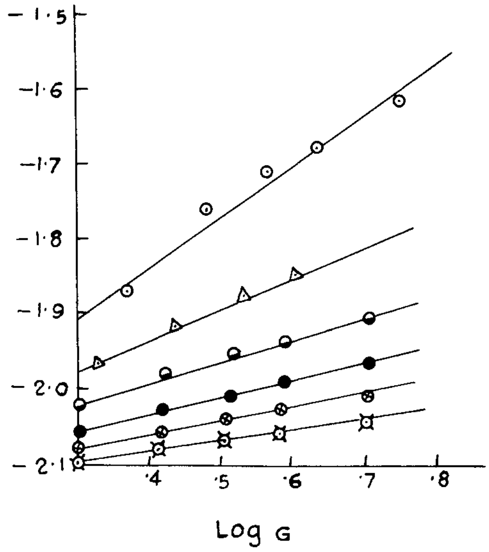

Fig. 7 Dependence of regression rate on the total mass flow rate for copolymer. ⊙ 5 sec; △ 15 sec; ◒ 25 sec; ● 35 sec; ⊗ 45 sec; ⛭ 55 sec.

It is found that $\dot m_f$ does not vary with time for a particular flow rate of the oxidizer. The values of the constants for polystyrene and copolymer are 0.25 and 0.35, respectively, for $G_o = 1.90$.

In order to evaluate $\dot r$, the duct radius r was measured for various combustion times t. Plots of $\log(r-A)$ against $\log t$ were found to be linear showing that the equation

$$r = A + K \cdot t^x \tag{25}$$

fits the data where A is the initial radius and K and x are constants. Values of K and x were determined graphically and $\dot r$ was obtained by differentiating Eq. (25) with respect to t so that

$$\dot r = Kxt^{x-1} \tag{26}$$

In this manner, r was determined for various values of G_o at different combustion times. The results are plotted in Fig. 2 for the two polymers.

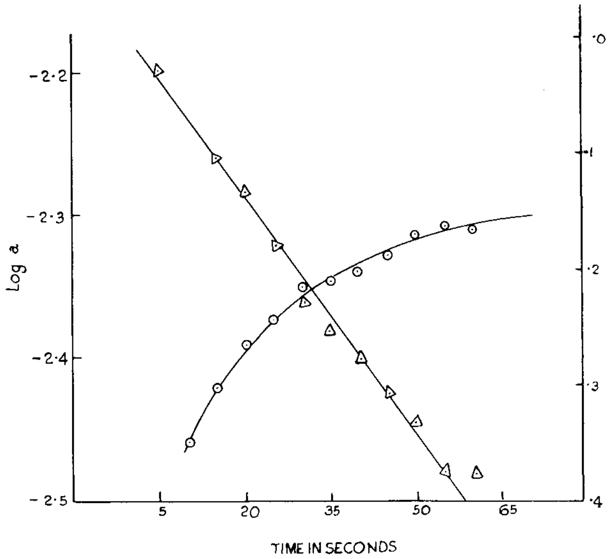

Fig. 9 Time dependence of a and n for polystyrene. △ n; ⊙ a.

According to Marxman[10] we have for cylindrical grains

$$\rho_f \bar{\dot r} = (D_o/D_{\rm avg})^{1.6} G_o K_1[1.25 + 2.5(D_o/D_{\rm avg})^{0.6} K_1 (L/D_o) + 2.18(D_o/D_{\rm avg})^{1.2}(K_1{}^2)(L/D_o)^2] \tag{27}$$

when radiative heat transfer is neglected. Figures 3 and 4 show that Eq. (27) is not satisfied by the data. We may now examine the results on the basis of the following equation from Smoot and Price[11]

$$\dot r = 0.023(G^{0.8}/\rho_f \lambda)(\mu/D)^{0.2} \ln[1 + (B\lambda/Pr^{2/3})] \tag{28}$$

according to which

$$\dot r D^{0.2} = aG^n \tag{29}$$

and

$$\dot r D^{0.2} = a' G_o{}^{n'} \tag{30}$$

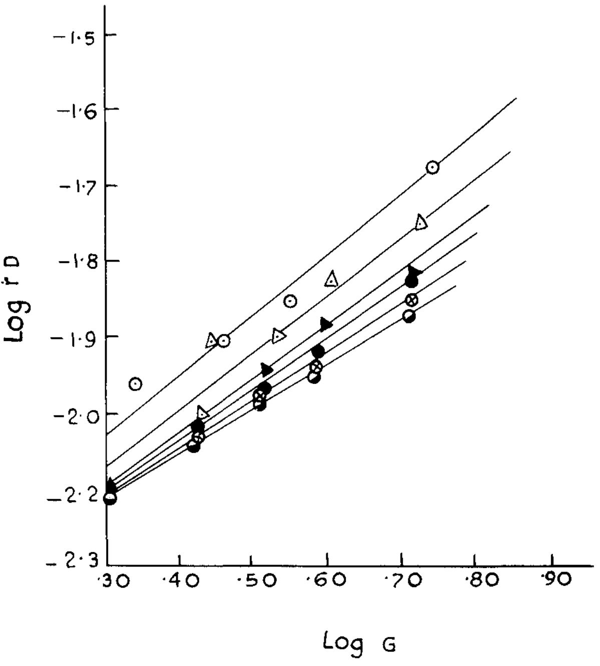

Fig. 8 Dependence of regression rate on the total mass flow rate for polystyrene. ⊙ 5 sec; △ 15 sec; ▲ 25 sec; ● 35 sec; ⊗ 45 sec; ◒ 55 sec.

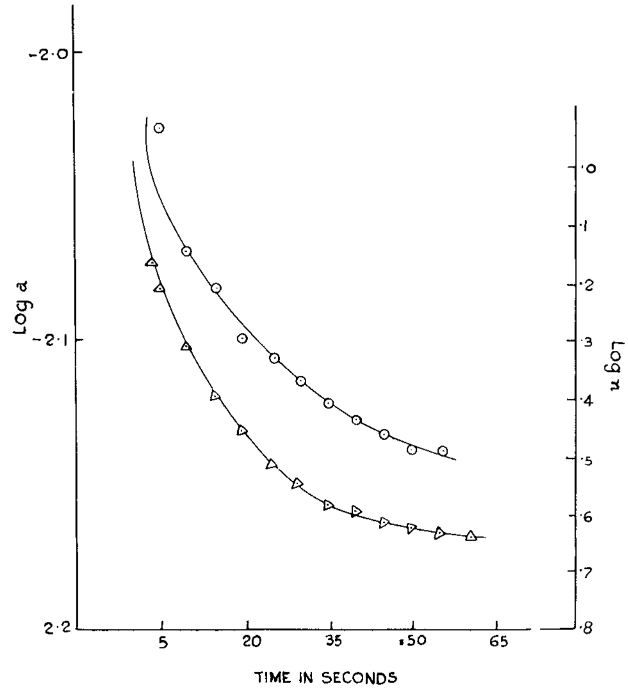

Fig. 10 Time dependence of a and n for copolymer. △ n; ⊙ a.

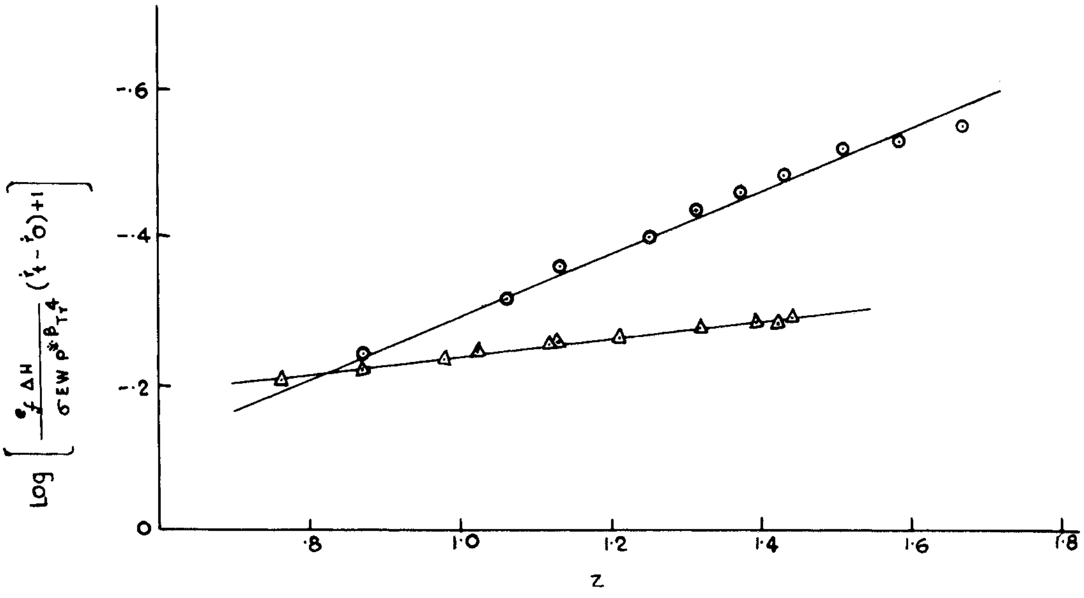

Fig. 11 Test of Eq. (23). ⊙ Copolymer; △ Polystyrene.

where

$$a = (0.023/\rho_f \lambda)\mu^{0.2}\ln[1+(B\lambda/Pr^{2/3})]$$
$$n = 0.8 \tag{31}$$

and

$$G = G_o + (4/D)(L\cdot\dot{r}\rho_f) \tag{32}$$

Figures 5–8 clearly show that Eqs. (29) and (30) are satisfied by the data. Both a and n depend on time, as shown in Figs. 9 and 10.

Results plotted in Fig. 2 show that the regression rate varies with time. This may be due to the radiative heat transfer from the flame zone to the unreacted oxidizer flowing through the duct, as suggested by Rastogi and Baijal.[3]

If this is so, Eq. (23) must be satisfied by the data, provided pressure is assumed to be constant. This is not unrealistic since mass flow of fuel in our case does not vary with time. However, to test Eq. (23), it is necessary to estimate $\dot{r}_o$ and the value of the quantity $[\rho_f \Delta H/\sigma\varepsilon_w p^{*\beta}T_r^4]$. These were determined in the following manner: $\dot{r}_o$ was estimated by 1) plotting $\dot{r}$ against t and extrapolating to zero time, and 2) by plotting $(r-A)$ against t and determining the slope at zero time. Both the methods yielded identical values of $\dot{r}_o$ within experimental error. The value of $[\rho_f \Delta H/\sigma\varepsilon_w p^{*\beta}T_r^4]$ was determined from the limiting slope of the plot of $(\dot{r}_o-\dot{r}_t)$ vs duct diameter at zero time. In order to check Eq. (23) $\log[(\rho_f \Delta H/\sigma\varepsilon_w p^{*\beta}T_r^4)(\dot{r}_t-\dot{r}_o)+1]$ was plotted against z. A straight line is obtained as shown in Fig. 11 which confirms Eq. (23). It follows from Fig. 12 that the magnitude of

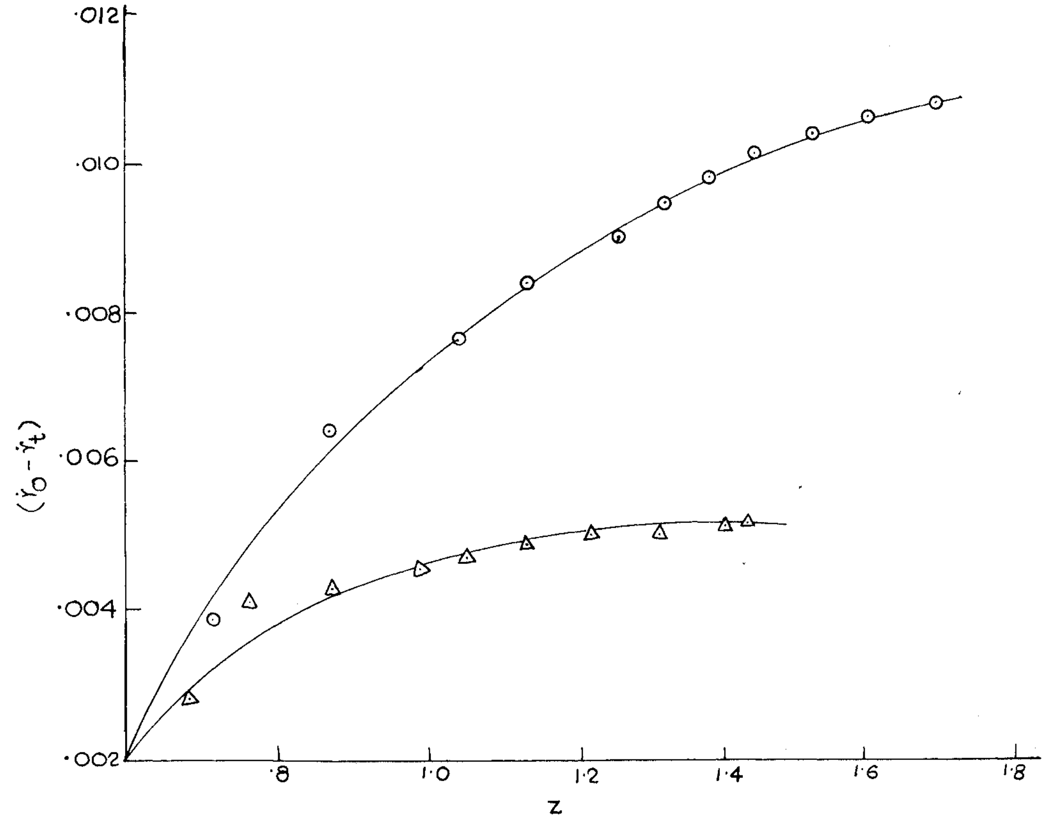

Fig. 12 Variation of $(r_o - r_t)$ with duct diameter of the grain. ○ Copolymer; △ Polystyrene.

$(\dot{r}_o - \dot{r}_t)$ is much larger for copolymer at a particular time as compared to the corresponding value for polystyrene. From Eq. (21) it follows that

$$(\dot{r}_o - \dot{r}_t) = (\sigma \varepsilon_w p^{*\beta} T_r^4 / \rho_f \, \Delta H)(1 - e^{-\alpha p z}) \tag{33}$$

Since quantities other than T_r^4 on the right-hand side of Eq. (33) would be of similar magnitude in the case of two polymers, $(\dot{r}_o - \dot{r}_t)$ should be a sensitive function of T_r since its fourth power occurs in Eq. (33). In order to test this point, flame temperature for polystyrene/O_2 and copolymer/O_2 system for $G_o = 0.7$ were measured by sodium line reversal technique and were found to be 1860 ± 20°C and 1970 ± 20°C. Since the flame temperature is higher for copolymer for the same flow rate of the oxidizer at a fixed time, the magnitude of $(\dot{r}_o - \dot{r}_t)$ for the copolymer should be higher. It is found that $(\dot{r}_o - \dot{r}_t)$ for the copolymer is 1.9 times the corresponding value for polystyrene. This ratio compares favorably with the ratio of the fourth power of the flame temperature which is 1.5. This further supports the validity of Eq. (23).

Conclusions

1) The regression rate varies with time for a fixed flow rate of oxidizer for copolymer/O_2 and polystyrene/O_2 systems.

2) The mass consumption rate of the fuel depends linearly on the square root of mass flow of oxidizer.

3) The equation $\dot{r}D^{0.2} = aG^n$ where a and n depend on time satisfies the data.

4) The data on time dependence of $\dot{r}$ satisfies Eq. (21) viz.,

$$\dot{r}_t = \dot{r}_o - (\sigma \varepsilon_w p^{*\beta} T_r^4 / \rho_f \, \Delta H)(1 - e^{-\alpha p z})$$

which proves the importance of radiative heat transfer in hybrid combustion.

5) The ratio of the magnitude of $(\dot{r}_o - \dot{r}_t)$ for copolymer and polystyrene is 1.9 which agrees with the ratio of the fourth power of flame temperature which is equal to 1.5.

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