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Rocket Propellant Combustion Studies in a Constant Volume Bomb

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Abstract—A constant volume window bomb has been used to measure the characteristic velocity (c^*) of rocket propellants. Analysis of the combustion process inside the bomb including heat losses has been made. The experiments on double base and composite propellants have revealed some (i) basic heat transfer aspects inside the bomb and (ii) combustion characteristics of Ammonium Perchlorate-Polyester propellants. It has been found that combustion continues even beyond the peak pressure and temperature points. Lithium Fluoride mixed propellants do not seem to indicate significant differences in c^* though the low pressure deflagration limit is increased with percentage of Lithium Fluoride.

SYMBOLS

A_s	Inside surface area of the bomb (cm²)
I_{sp}	Specific impulse (secs)
C_F^0	Ideal thrust coefficient
C_v	Specific heat at constant volume (cal/gm °K)
c^*	Characteristic velocity (cm/sec)
h	Heat transfer coefficient (cal/cm² sec °K)
h_s	Steady state heat transfer coefficient (cal/cm² sec °K)
H	Heat of combustion (cal/gm)
m_{in}	Mass of inert gas inside the bomb (gm)
m_f	Mass of the propellant
M	Nondimensional number (see equation 5)
$\mathscr{M}_{in}$, $\mathscr{M}_f$	Initial and final molecular weights of gases
p_{in}	Initial pressure of the filling gas (Kg/cm²)
p_{max}	Maximum pressure of the (product + inert) gas (Kg/cm²)
$\mathscr{R}$	Universal gas constant
R	Gas constant of gases in the bomb
t_{peak}	Time for peak pressure to attain (sec)
t_{ign}	Characteristic combustion time (sec)
$T_{v,ad}$	Maximum adiabatic temperature at constant volume (°K)
$T_{p,ad}$	Maximum adiabatic temperature at constant pressure (°K)
T_{in}	Initial temperature of the filling gas (°K)
V	Volume of the bomb (cm³)
γ	Specific heat ratio
$\Gamma(\gamma)$	$\sqrt{\gamma}\left[\frac{2}{\gamma+1}\right]^{(\gamma+1)/(2\gamma-2)}$

1. INTRODUCTION

The constant volume method of evaluation of ballistic properties of propellants had the origin in the evaluation of properties of gun propellants. Since gun propellants experience pressures of the order of 1000–5000 atmospheres, the bomb method used for rocket propellants also considered using these high pressures. At these pressures real gas effects dominate and hence the equation of state for real gases is used. The constant 'b' in equation

$$p(v - b) = n\mathscr{R}T \quad \text{where } n = \text{number of moles} \tag{1}$$

accounts for 'co-volume' effect. This constant is determined from experiments and then flame temperatures are evaluated after measuring the peak bomb pressures (~1000 atms) for a known mass of the propellant. This is essentially the technique used by some investigators (Every and Thieme (1965), Fayon and Goldstein (1966), Iwama *et al.* (1967)) subsequent to Griffin *et al.* (1959), who proposed and used it for the first time. Thus the reason for using such a procedure involving very high pressures and so involving the experimental estimation of the 'co-volume' appears to be essentially historical. If there are other reasons, they have not been discussed by any of the previous authors.

In the present work, the essential idea is to keep the pressure levels at about the rocket operating pressures (≈100 atms) so that co-volume effect need not be considered. This however alters the situation experienced by the earlier workers (Griffin *et al.* (1959) and Iwama *et al.* (1967)). Since the pressures were very high, the burning rates (or consumption rates) were very large and time for combustion were very small-typically 2–4 msecs as in Griffin *et al.* (1959), of the order of 20–30 msecs as in Iwama *et al.* (1967) and 0.2–0.3 secs as in Fayon and Goldstein (1966). During

this period of pressure rise, there will be temperature rise and so heat losses to the wall will be occurring. These heat losses can be expected to be insignificant, not insignificant and certainly significant for the above experiments respectively. The time scales in the present investigation are of the order of 0.3–1 sec or more. Hence analysis is needed to take account of the heat losses.

Though from the above consideration, the advantages gained by lowering the pressure levels appear to have disappeared some new features of combustion and heat transfer occurring in the bomb have been uncovered as a consequence. Probably these may be occurring even in the case of earlier investigations and hence may require a fresh look at the earlier experiments.

2. EARLIER WORK

Iwama *et al.* (1967) in an effort to improve upon the work of Griffin *et al.* (1959) have tried to calculate the co-volume from equilibrium computations of composition. The relevance of the use of such estimates in the highly non-equilibrium situations present during the very fast combustion is questionable. Also the estimates of co-volume do not seem to correlate well with the loading density, a fact which has been assumed by Iwama *et al.* (1967). It appears best to estimate '*b*', the co-volume from actual experiments as has been done by Griffin *et al.* (1959). This procedure seems to have been also used by Every and Thieme (1965) for the evaluation of the ballistic properties of liquid oxygen and methane. Fayon and Goldstein (1966) use the constant volume bomb technique to obtain the burning rate law of the propellants. In their analysis used to obtain the burning rates from the pressure-time traces, an assumption that the temperature of the gases in the chamber is constant has been made. This assumption is of somewhat doubtful value. Their results on mass balance, however, seem to check with those obtained by the deduced burning rate law.

3. THEORY

The heat balance for the gas in the bomb at any time can be written as

$$mH = (m_{in} + m)C_v(T - T_{in}) + \text{Losses} \quad (2)$$

where m is the mass of propellant burnt at any time. The losses can be written as

$$\text{Losses} = A_s\int_0^t h(T - T_{in})\,dt \quad (3)$$

The heat transfer coefficient, h in equation (3) can depend on time quite strongly because of the transient nature of the combustion.

If we now equate the heat release to the heat absorbed under adiabatic conditions, we have

$$mC_v(T_{v,ad} - T_{in}) = (m_{in} + m)C_v(T_{\max} - T_{in}) + A_s h_s\int_0^t \frac{h}{h_s}(T - T_{in})\,dt$$

If we perform the integration up to the peak pressure conditions we can rewrite the above equation as

$$\frac{T_{v,ad}}{T_{in}} = 1 + \left(\frac{m_{in} + m_f}{m_f}\right)\left(\frac{T_{\max}}{T_{in}} - 1\right) + \left(\frac{h_s A_s T_{\text{peak}}}{m_f C_v}\right)\int_0^1 \frac{h}{h_s}\left(\frac{T}{T_{in}} - 1\right) d\left(\frac{t}{t_{\text{peak}}}\right) \quad (4)$$

Validity of the equation (4), implies that the complete propellant mass would have burnt at the peak pressure, (see section 5.1 for further discussion).

It will be noticed that equation (4) consists of non-dimensional terms alone. We define

$$M = \frac{h_s A_s t_{\text{peak}}}{m_f C_v} = \frac{h_s A_s}{(m_f C_v/t_{\text{peak}})} \quad (5)$$

where M is nondimensional. This number characterises the ratio of heat loss rate to heat production rate as is expressed in the second equality. $M \to 0$ implies that the heat loss effects are insignificant i.e. approach to adiabatic conditions takes place. M can be made small by increasing the mass of the propellant inside the bomb or by so burning it that t_{peak} is made small. It also appears preferable to choose a bomb such that minimum surface area for a given volume is obtained. This naturally leads to a spherical bomb.

In the present work, however, a conventional bomb has been used as difficulty was experienced in obtaining a spherical bomb. The heat transfer coefficient can be reduced by making the bomb inside material as insulating.

The equation (4) can be recast as

$$T_{v,ad} = \frac{V}{m_f \mathscr{R}}(p_{\max}\mathscr{M}_f - p_{in}\mathscr{M}_{in}) + M\int_0^1 \frac{h}{h_s}\left(\frac{pV}{(m + m_{in})R} - T_{in}\right) d\left(\frac{t}{t_{\text{peak}}}\right) \quad (6)$$

In the experiments which have been made by earlier workers as well as the present one, the pressure-time trace is the one used for obtaining the adiabatic flame temperature. And it is probably the only meaningful method for obtaining the adiabatic temperature. A primary reason for this is as follows. In the heat loss integral of equation (6), we notice that both the mass of the gas at any time $= m_{in} + m$ and h/h_s depend on time. If we desire to burn the propellant in any arbitrary geometry, it will be almost impossible to estimate m. Hence the evaluation of the heat loss integral will be quite involved. Also one should expect that any such effects should be reflected in the pressure-time trace. It appears better, therefore, to replace the heat loss integral by a pressure-time integral as below.

$$T_{v,ad} = \frac{V}{\mathscr{R}m_f}(p_{\max}\mathscr{M}_f - p_{in}\mathscr{M}_{in}) + f\left[\frac{\int_0^{t_{peak}}(p - p_{in})\,dt}{p_{\max}}\right] \quad (7)$$

It may be pointed out that even though the replacement is arbitrary, the functional form of the heat loss integral has been left undefined and hence no generality is lost. We can define

$$t_{ign} = \int_0^{t_{peak}}(p - p_{in})\,dt/p_{\max} \quad (8)$$

It may be noted that t_{ign} takes on a character essentially the same as M. Thus

$$T_{v,ad} = \frac{V}{\mathscr{R}m_f}(p_{\max}\mathscr{M}_f - p_{in}\mathscr{M}_{in}) + f(t_{ign}) \quad (9)$$

$\mathscr{M}_f$ in the equation (9) is evaluated from the expression for the average molecular weights of mixtures of gases, namely

$$\mathscr{M}_f = \left\{\frac{m_f}{\mathscr{M}_p(m_f + m_{in})} + \frac{m_{in}}{\mathscr{M}_{in}(m_f + m_{in})}\right\}^{-1}$$

where $\mathscr{M}_p$ is the molecular weight of the products of combustion. In the case of solid propellants, $\mathscr{M}_p$ usually varies from 24–26. Hence $\mathscr{M}_f$ will lie between 25–27. Now we adopt the procedure which parallels that used by Griffin *et al.* (1959). The pressure-time trace for a number of masses of propellants and methods of burning are obtained so that peak pressures for a wide range of t_{ign} values are obtained. These data are then curve fitted and the results for $t_{ign} \to 0$ lead to the determination of adiabatic combustion temperature at constant volume. Rocket combustion takes place, however, at near constant pressures instead of constant volume. The above results have, therefore, to be converted to those at constant pressure.

Following Griffin *et al.* (1959), we obtain

$$T_{p,ad} = \frac{T_{v,ad}}{\gamma} + T_{ref}(1 - 1/\gamma) \quad (10)$$

The above relation assumes that $\Delta n\mathscr{R}T \ll Q_V$, where Δn is the change in the number of moles from reactants to products and Q_V = enthalpy of the gases at constant volume. For most reactions of interest it turns out that the above condition is satisfied. From the values of $T_{p,ad}$ so obtained one obtains the characteristic velocity as

$$c^* = \sqrt{RT_{p,ad}/\Gamma(\gamma)} \quad (11)$$

It is to be recognized that estimates of γ and molecular weight of the products of combustion are to be obtained from other sources like computation of equilibrium products of combustion. Generally these values do not vary significantly with pressure for conventional solid/liquid propellants.

The specific impulse can be obtained by estimating C_F^0 for a given rocket motor geometry and p_c, p_e etc. as

$$I_{sp} = C_F^0 c^*/g \quad (12)$$

4. EXPERIMENTAL SET-UP AND DATA REDUCTION

Figure 1 shows the schematic view of the set up used for the experiments. The details of the bomb assembly are given elsewhere (Mukunda and Raghunandan (1974)). A strain guage transducer was used for making transient pressure measurements. A Pt-Pt-13% Rh thermocouple (0.1 mm diameter wire, bead being made a flat disc, 0.5 mm dia and 0.1 mm thick) was used for the transient temperature measurements. The rise time of both the devices was sufficiently small compared to transient periods in the experiments. The outputs from the pressure transducer and thermocouples were amplified and recorded on a visicorder at paper speeds of 25 mm/sec or 50 mm/sec. Ignition was affected by covering the samples with a thin Nichrome wire and passing a direct current of about 500–600 m amps at 12 volts.

Data analysis consists in measuring pressures at different intervals of time and curve fitting the

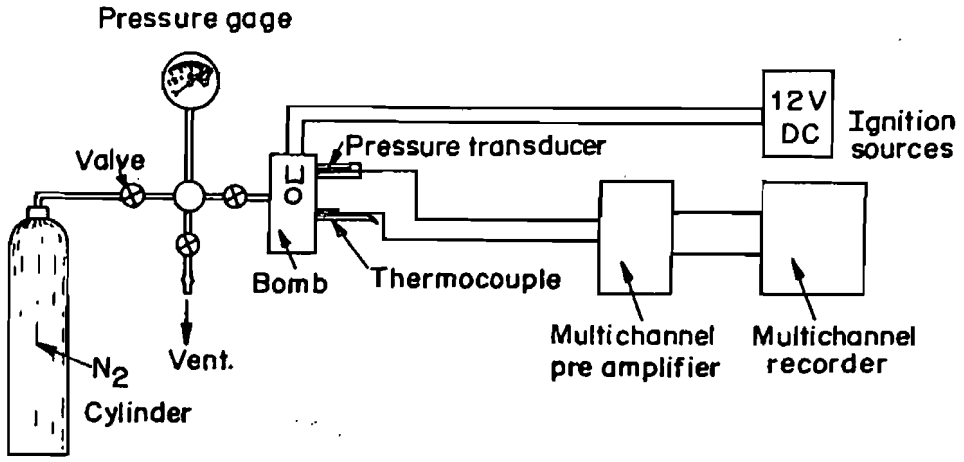

FIG. 1. Schematic of the set-up.

data into a polynomial for p in terms of t. Use of (8) gives t_{ign}. A plot of

$$\frac{V}{\mathscr{R}m_f}(p_{\max}\mathscr{M}_f - p_{in}\mathscr{M}_{in}) \text{ vs } t_{ign}$$

is used for extrapolation purposes. Also a curve fit of this relation leads to the determination of $T_{v,ad}$.

In order to obtain samples with varying t_{ign} different geometries of the propellant were used some being partly inhibited. Figure 2 shows the various geometries used for the purpose along with the t_{ign} achievable in each case. In order to account for the heat addition due to combustion of ignition wire, estimates were made of the heat of combustion per unit weight of the wire and it was found that 1 mg wire would amount to 4.0 mg of the propellant (Double Base). The overall accuracies of the experiments may be set at about 3 per cent.

5. RESULTS AND DISCUSSION

5.1 *Mass burnt at peak pressure*

A typical trace of the pressure is as shown in Figure 3. The various characteristics of the trace are shown on the figure. The final pressure (when the final temperature is equal to the initial temperature) attained as $t \to \infty$ is much higher than p_{in} and is given by

$$p_f = \left(\frac{m_{in} + m_f}{m_{in}}\right) p_{in} \frac{\mathscr{M}_{in}}{\mathscr{M}_f} \tag{13}$$

In order to check whether combustion would be complete at the time for peak pressure, measurements of the time for peak pressure and the death of visible flame were also made using an electronic timer. The timer was started when the ignition switch and recorder were turned on and it was

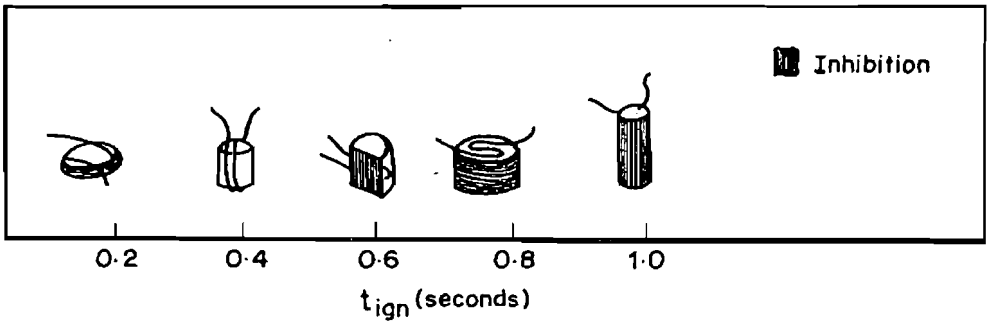

FIG. 2. Methods of arranging the sample to obtain a variety of initial pressure rises (or t_{ign}).

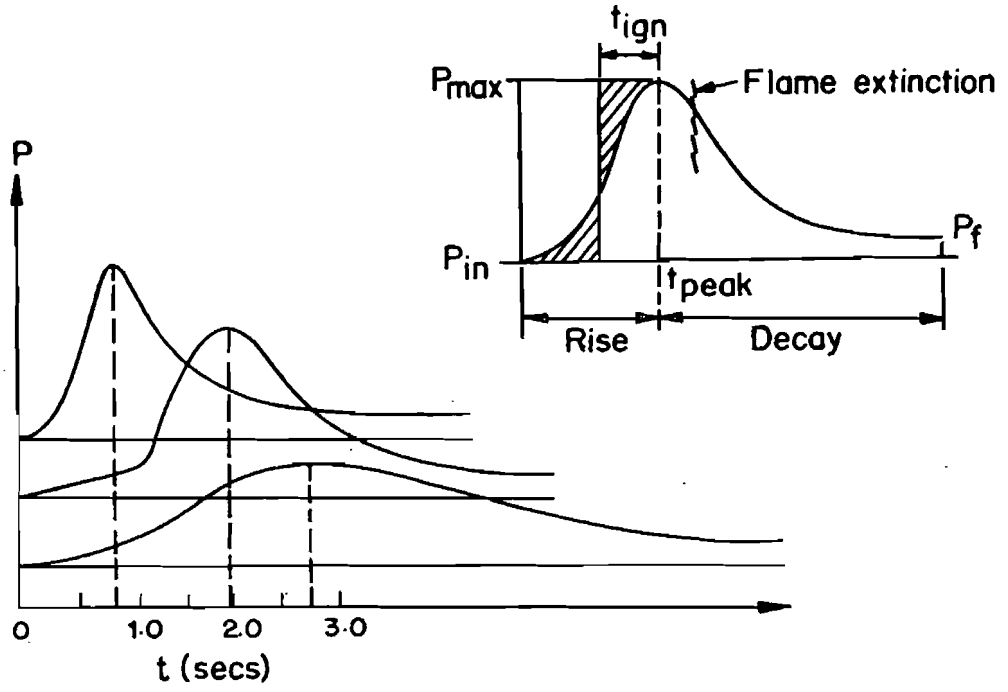

FIG. 3. A typical set of pressure time traces with nomenclature.

stopped when the flame disappeared. The results are shown in the Table I.

It is seen that the flame is present in every case beyond the peak point. This fact was confirmed in a large number of experiments. The implication of this fact is that it cannot be taken that all the mass disappears at the peak pressure (and peak temperature as seen subsequently). Fayon and Goldstein (1966) show from their work which involves burning times of the same order as the present that mass balance calculations tally when computed from the deduced burning rate data. From this it appears that the mass burnt after the peak may not be significant.

TABLE I

Test no.	Time for peak, secs.	Time for flame extinction, secs.	Pressure at extinction/ pressure at peak
3/22–7	0.5	0.85 ± 0.1	0.78
4/22–7	0.5	0.8 ± 0.1	0.75
8/22–7	2.35	2.85 ± 0.1	0.66
1/24–7	0.475	0.85 ± 0.1	0.73

5.2 *Heat loss beyond the point of peak pressure*

If heat loss alone dominated, the process beyond the peak pressure or some point on the decaying part of the *p-t* trace, we have

$$\frac{d}{dt}\{(m_{in} + m_f)C_v T\} = -hA_s(T - T_{in}) \quad (14)$$

Rewriting this equation in terms of p we obtain

$$C_v \frac{d}{dt}\left(\frac{pV\mathscr{M}_f}{\mathscr{R}}\right) = -hA_s\left(\frac{pV\mathscr{M}_f}{\mathscr{R}(m_{in} + m_f)} - T_{in}\right)$$

If we solve this we get

$$p = p_g + (p_{max} - p_g) \times \exp\left(-\frac{hA_s}{(m_{in} + m_f)C_v}(t - t_{peak})\right)$$

$$t \geqslant t_{peak}$$

where $p_g = (m_{in} + m_f)\mathscr{R}T_{in}/\mathscr{M}_f V$.

Thus the plot of $\ln (p - p_g)/(p_{max} - p_g)$ *vs* $(t - t_{peak})$ should lead to a straight line. Figure 4 shows the plots for a number of cases. It is seen that instead of a single straight line, there seem to be

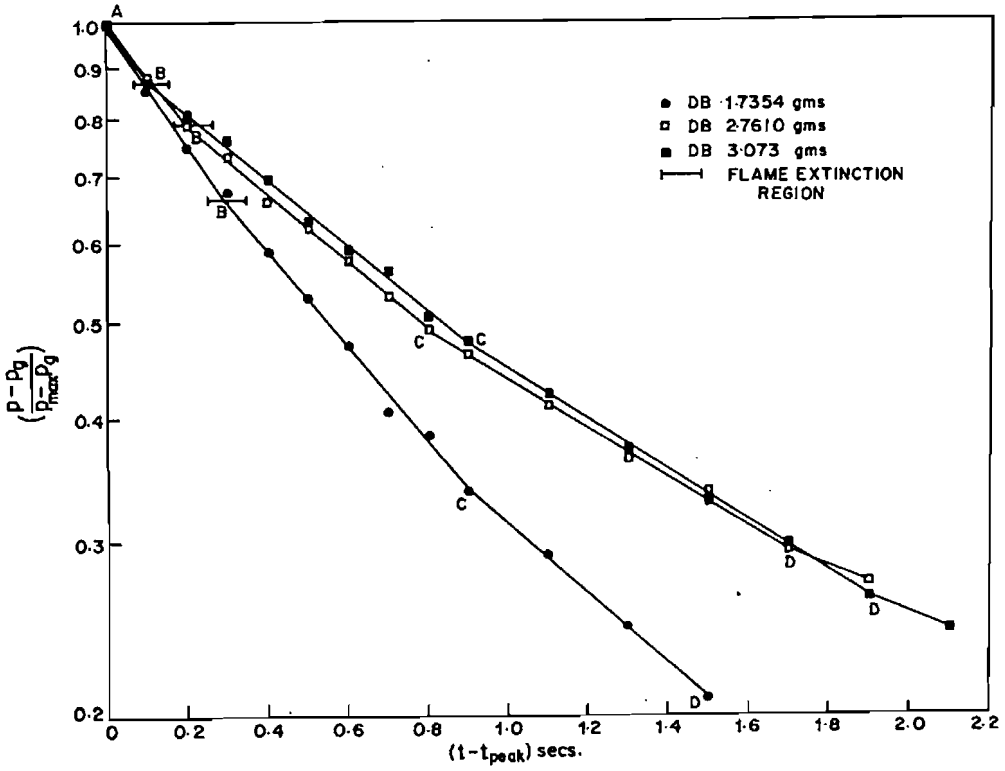

FIG. 4. Pressure-time curves during decay period.

a number of lines with discontinuous slopes. Though one can state that the points belong to some general curve, there appears good justification for identifying the straight line regions with distinct slopes. In fact, many other curves not shown in the figure also could be classified similarly. The first break in the curve can be identified with the extinction of the flame. The slopes of the curves are decreasing with increasing time. This feature is somewhat inexplicable. The decrease in the slope even at the region of flame extinction does not appear correct. The slope, we expect, should be larger beyond B since in the region AB we have heat release which terminates at B. The cause for this and the change in slopes at C, D etc. appear probably to be due to the change in transport properties i.e. change in h/C_v due to decrease in temperature with respect to time.

5.3 *Temperature-time curves*

In order to obtain information on the temperature inside the bomb, temperature traces were obtained. A typical trace is shown in Figure 5a. It is seen that in the rising part the trace follows the pressure-time curve. However, beyond this point the temperature decays very slowly for a large period of time and then drops rather suddenly. The position of the thermocouple bead in this experiment is also shown therein. The temperature which is measured, in principle, refers to a point or a region rather than the bomb as a whole, for the bead placed next to the propellant would measure much higher temperatures than at other stations. If however, mixing was intense in the whole region, then we would expect that temperature over a large portion would be same. Convective mixing is a principal mode of mixing and the typical time scales of mixing can be obtained as L/v, where L is the length the gases have to traverse and v is the velocity of the gases. Typically $L \sim 5$ cms and $v \sim 100$ cm/sec. This leads to mixing time scale of about 50 m secs. The typical transient rise times vary from 300 m secs to 600 m secs. Hence we can expect that the temperature recorded really belongs to an 'average' temperature of the bomb. Also the rise characteristic of temperature is similar to that of pressure. The start of the temperature signal occurs at the same time as of pressure signal in every case. These give credence to the fact that gases are homogeneous with respect

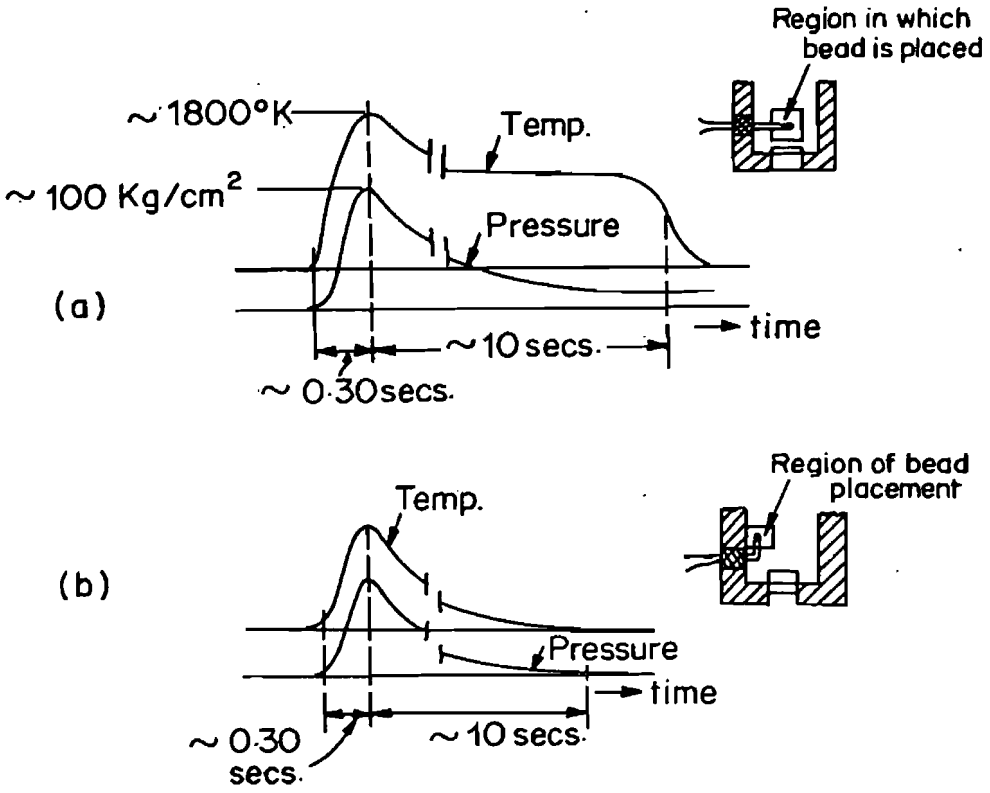

FIG. 5a and b. Typical pressure and temperature traces.

to temperature over the region of measurement of temperature. In the decay part we expect that temperature and pressure to be proportional to each other. However the temperature seems to decay at much slower rate than the pressure. The position of the thermocouple seemed to matter in this regard. When the bead was positioned closer to the wall, the temperature-time trace followed the pressure-time trace as shown in Figure 5b which is what is to be expected. The cause for the difference as in Figure 5a was hypotheized as being due to the condensation of the water vapour (which is a principal product of combustion) on the thermocouple bead, thus preventing the record of the true gas temperature. The water vapour would be subjected to the various phases of nucleate and film boiling and when the water vaporized completely true gas temperature would be recorded. In case (ii) reflected in Figure 5b, condensation was probably not occurring and hence the profiles of temperature and pressure are similar. Further experiments are underway to verify the hypothesis.

5.4 *Combustion of double base and composite propellants*

The propellants that have been studied are indicated in Table II. The table also indicates the bomb initial conditions during the experiment.

From Table II it is clear that the low pressure deflagration limit is appreciably large for LiF catalysed propellants. These propellants would not ignite or sustain combustion inside the bomb at pressures roughly indicated in Table II. These results were obtained also by Dhameja (1973) earlier in burning rate studies using a strand burner.

Figure 6 shows the plot of $V/m_f\mathscr{R}(p_{\max}\mathscr{M}_f - p_{in}\mathscr{M}_{in})$ as a function of t_{ign}. It is seen that the data of D.B. propellants correlate very well leading to a flame temperature 2500 ± 50 °K. The $T_{v,ad}$ of all the composite propellants is about 2550 ± 50 °K with the exception of BI,1 which has a value of 2200 ± 50 °K. The curves for (BI,1), (BI,2), and (BI,3) indicate that the c^* values (or flame temperatures) are increased by increase in the initial pressure at which combustion is initiated.

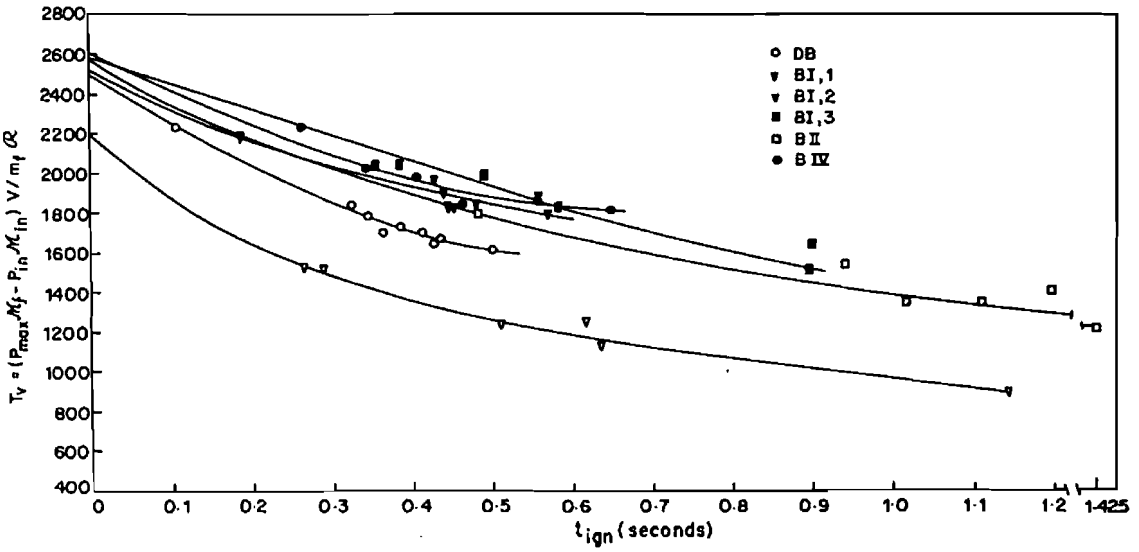

FIG. 6. Plot of T_v vs t_{ign} for double base (DB) and composite propellants.

TABLE II

Propellant	Composition (per cent by weight)		Initial conditions in the bomb
1. DB	—		1 atm. Air
2. BI,1	AP	70	1 atm. Air
BI,2	PDR111	18	6 atm. N_2
BI,3	Styrene	9	13 atm. N_2
	DOP	3	
3. BII	AP	69.5	
	PDR111	18	
	Styrene	9	6 atm. N_2
	DOP	3	
	LiF	0.5	
4. BIV	AP	68.5	
	PDR111	18	
	Styrene	9	13 atm. N_2
	DOP	3	
	LiF	1.5	

There was significant carbon deposit particularly at low pressures pointing to the incomplete combustion of the already fuel rich composition at lower pressures. The results are not very different for firings at 6 atms and 13 atms showing that the effect of initial pressure has become small. The results of BI, BII, and BIV obtained at 6 atm and above indicate that the c^* values are not very different between various samples. This implies that LiF has marginal effect on the specific impulse of the propellant.

6. CONCLUSIONS

Some of the significant conclusions of the present work are the following:

1) Criteria for the design of a constant volume bomb with peak pressures of the order of rocket operating pressure have been obtained.

2) Combustion of the propellant inside the bomb proceeds even beyond the point of peak pressure.

3) The heat loss traces seem to indicate either significant heat release or strong variation of the transport properties of the gases during the time after all the mass has been burnt.

4) The characteristic velocities of composite Polyester AP propellants do not seem to depend on the extent of LiF in AP (when mixed with LiF).

5) Considering the implications of the conclusion (2) above, it appears that the impulse bomb of the above kind is better suited to comparing the performance (i.e. c^*) between given propellants rather than evaluating the actual performance.

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