Engineering Notes

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Combustion of Phenol-Formaldehyde Composite Propellants

H.L. Girdhar* and A.J. Arora†
The University of Kashmir, Srinagar (J&K), India

Introduction

THE study of the effects of various parameters on burning rate can contribute significantly in understanding the combustion mechanism of propellants. The use of phenol-formaldehyde-type Bakelite resin as a possible binder fuel has been reported by Rastogi and Ouseph.[1] The present paper describes the effect of various oxidizers, fuel-oxidizer ratio, initial temperature and additives on the burning rate of composite propellants based on phenol-formaldehyde polymer.

Experimental

Materials: Phenol-formaldehyde casting resin was prepared as described previously.[2] The oxidizers and additives used in this study were of good quality. The particle size of these was in the range 200-250 mesh.

Procedure: The strands of different polymer-oxidizer composition were extruded by applying constant pressure. Carbon black (concentration 0.2%) was used as an opacifying agent. Cured strands were coated with 0.1 mm-thick layer of sodium silicate inhibiter, except in the case of propellants containing ammonium salts, where phenol-formaldehyde resin was used as inhibitor because sodium silicate reacts with these oxidizers and causes perforations in the inhibiter layer due to evolution of ammonia gas. The strands were about 6 cm in length and 0.65 cm in diameter.

The burning rates were measured in a one-atmosphere thermostat by strand burning technique. The maximum fluctuations in temperature were ± 0.1°C up to 35° C and ± 0.5°C for higher temperatures. The reproducibility of the results was within ± 3 percent. The heat of combustion of the polymer and heats of explosion of the propellants in nitrogen atmosphere (1 atm) were determined by bomb calorimetric technique. The densities of propellants were measured by a mercury pyknometer.[2]

Results and Discussion

The experimental results are given in Tables 1 and 2. As seen from Fig. 1 the maximum linear burning rates are obtained at 75 percent by weight of each of the oxidizers NH_4ClO_4, $KClO_4$, and 73.5 percent of $NaNO_3$. In the case of a propellant having KNO_3 the maximum burning rate has been reported[1] to occur at 75% of the oxidizer. Propellants containing NH_4NO_3 oxidizer did not burn at any composition.

Effect of Temperature: The temperature dependence of burning rate of propellants has been described by the relation[3]

$$r = \frac{Cp^n}{T_s - T_0} \tag{1}$$

where T_0 is the initial temperature, T_s represents the surface temperature of the propellant and r is the linear burning rate. For a particular propellant at constant pressure the quantity Cp^n will be constant. Thus plot of $1/r$ vs T_0 should be linear. The experimental data of burning rate fit the preceding equation (Fig. 2). The surface temperatures calculated from the slope and intercept of these plots are given in Table 2. Figure 3 shows that the burning rate decreases linearly with surface temperature. This is in agreement with the findings of Summerfield et al[4] that the burning rate of a propellant increases when the surface temperature is depressed.

Activation Energy of Burning Process: The combustion process of a composite propellant involves 1) decomposition of oxidizer to give gaseous products 2) formation of redox flame from the pyrolysis products of oxidizer 3) the pyrolysis of binder and 4) the gas phase exothermic reaction of the pyrolysis products of oxidizer and binder leading to continuous burning. Considering the preceding mechanism the activation energy of this overall process would be the sum of 1) activation energy of decomposition of the propellant which involves the first three steps and 2) the activation energy of the last step which involves a continuous burning process. The former can be computed from the decomposition kinetics data at various temperatures which could initiate ignition of propellant, while the latter has been calculated from the burning rate data by following consideration. As seen from Eq. (1) the surface temperature, T_s is the temperature at which the burning rate would become infinite. Therefore, the burning rate is assumed to follow the Arrhenius equation

$$r = Ae^{\frac{E}{R(T_s - T_0)}} \tag{2}$$

From the plots of $\log r$ vs $(1/T_s - T_0)$ the values of activation energy of burning process and prefactor A were calculated and these are summarized in Table 2.

Role of Additives: The effect of various additives (3% by weight) on burning rate was investigated. It was found that SnO and carbon black increase the burning rate in all types of propellants, Fe_2O_3 is effective only in case of propellants based on KNO_3, MnO_2, and CuO are effective in propellants containing NH_4ClO_4, $KClO_4$, and KNO_3. The role of additives in affecting the burning rate may be due to their

Table 1 Effect of initial temperature on burning rate of propellants

Temperature (°C)	Burning rate (cm/sec)			
	Ammonium perchlorate (77.5% by wt)	Potassium perchlorate (75% by wt)	Sodium nitrate (73.5% by wt)	Potassium nitrate[a] (75% by wt)
16				0.445
25	0.181	0.275	0.307	0.453
35	0.183	0.290	0.285	0.465
45	0.186	0.296	0.294	0.473 (at 46°C)
55	0.189	0.285	0.287	0.485
65	0.190	0.295	0.298	0.495
75	0.193	0.301	0.305	

[a] Data taken from Ref. 2.

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*Reader, Department of Chemistry.

†Junior Research Fellow, Department of Chemistry.

Table 2 Thermal and kinetic properties

Propellant System	Oxidizer (wt %)	Density (gm/ml)	Heat of explosion (cal/gm)	Surface temperature (°K)	Activation energy (k cal/mol)	Prefactor (cm/sec) × 10^2
Binder			6948[a]			
Binder/ammonium perchlorate	77.5	1.569	1245	1114	1.777	6.032
Binder/potassium perchlorate	75	1.766	1104	878	1.107	10.520
Binder/sodium nitrate	73.5	1.735	912	954	1.356	9.878
Binder/potassium nitrate	75	1.578	763	784	0.967	16.62

[a] Heat of combustion.

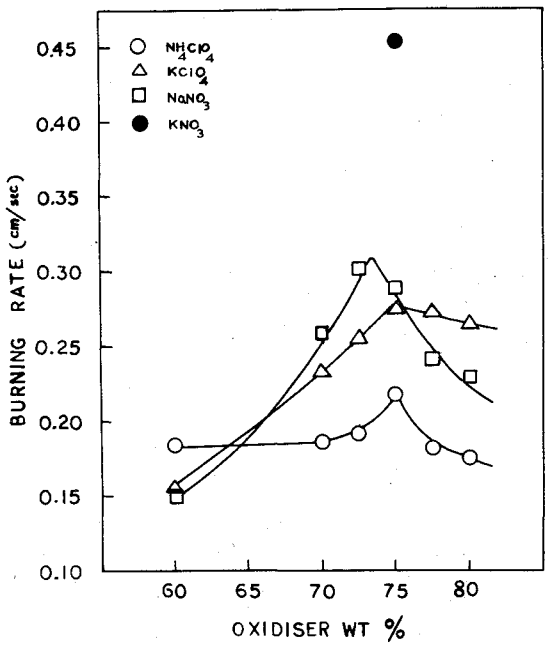

Fig. 1 Dependence of burning rate on composition.

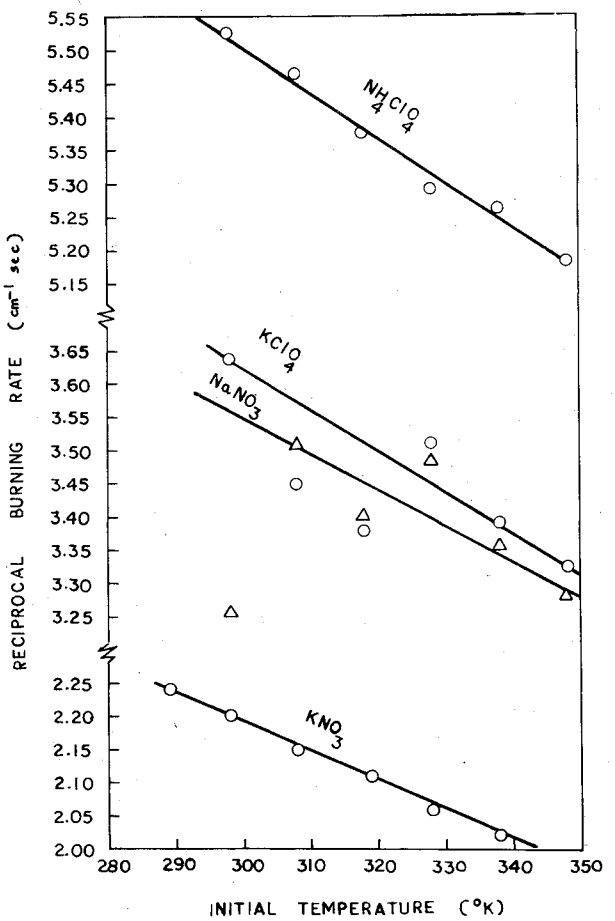

Fig. 2 Effect of initial temperature on burning rate.

catalytic action in the pyrolysis of either the polymer or the oxidizer. Very little is known about the catalytic action of metal oxides in the thermal degradation of polymers. Since metal oxides are effective electron donors, therefore, these play an active role in oxidative degradation of polymers by acting as oxygen exchangers.[5] The pyrolysis study of a variety of polymers carried out by Cohen et al[6] has revealed that the pyrolysis kinetics of binder have little effect on the burning rate in their two temperature model of combustion of composite propellant. Therefore, it would not be important whether the mechanism of pyrolysis of the binder is thermal or oxidative. Consequently, the kinetics of pyrolysis of the oxidizer would be playing a significant role in influencing the burning rate. The decomposition of these oxidizers has been found to be accelerated[7] in presence of various metal oxides and carbon black which may thus be increasing the burning rate of propellants.

Heats of Explosion: The burning rate is found to decrease linearly with heat of explosion for propellants based on different oxidizers (Fig. 3). This shows that at atmospheric pressure, the thermal flux from propellant flame has less direct influence on the burning rate than do the oxidizer kinetics.

Conclusions

It can be concluded that initial temperature, surface temperature, activation energy and heat of explosion influence the burning rate. Metallic oxides increase the burning rate by

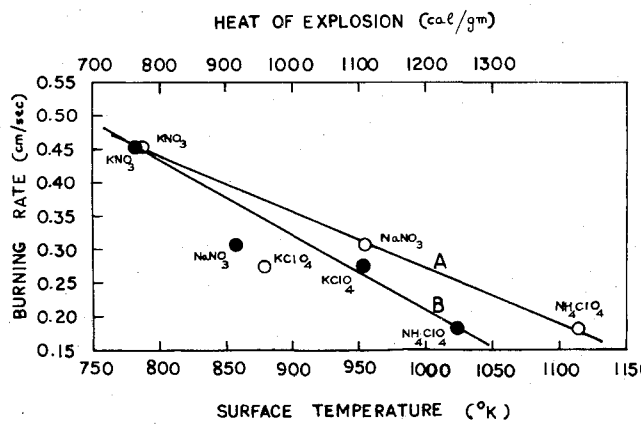

Fig. 3 A. Plot of surface temperature vs burning rates. B. Plot of heat of explosion vs burning rate.

affecting the kinetics of pyrolysis of oxidizers in composite propellants.

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Relationship between Coast Arc Length and Switching Function Value during Optimization

W.T. Fowler*
University of Texas at Austin, Austin, Texas
and
P.M. O'Neill†
McDonnel Douglas Aircraft Co., St. Louis, Mo.

Introduction

In the determination of optimal low-thrust interplanetary trajectories containing a coast arc, several procedures have been developed for handling the coast arc. These procedures usually involve either 1) the guessing of and iteration on the coast arc entry and exit times, t_1 and t_2 respectively, or 2) the use of a switching function, $\Gamma(t)$, to determine t_1 and t_2. Most procedures based on iteration on t_1 and t_2 do not use switching function information while most procedures based on the switching function do not employ iteration on t_1 and t_2.

The procedure described uses both the switching function and information equivalent to t_1 and t_2 (the length, T_0, and center, t_c, of the coast arc are used). The problem is formulated as a two-point boundary-value problem and guesses are made for all unknown initial states and Lagrange multipliers. Then initial guesses are made for t_c and T_0.

A standard perturbation-type optimization procedure (Refs. 1-5) is used to find the unknown initial states and multipliers with T_1 held constant. During each iteration, $\Gamma(t)$ is monitored, but it does not control the coast arc. Both T_0 and t_c are held constant until the unknown initial conditions have been converged. Then, t_c is shifted so that the values of the switching function $\Gamma(t_1)$ and $\Gamma(t_2)$ become equal. This equalization or balancing procedure usually takes only two or three iterations to reconverge the trajectory and produces a value of the switching function which will be called Γ_{BAL} ($\Gamma_{BALANCED}$). Figure 1 shows a typical switching function just prior to balancing. The switching function for the reconverged "balanced" trajectory will differ somewhat from the switching function prior to balancing, but usually the differences are small. After two different values of Γ_{BAL} have been obtained corresponding to two differing values of T_0, a linear extrapolation can be made to determine the optimal value of T_0. The fact that the Γ_{BAL} vs T_0 graph is linear was discovered during a series of optimization runs. It had not been planned to use the Γ_{BAL} vs T_0 plot to predict the optimal coast arc length, but when the linearity of the plot was discovered, it was used.

An outline of the procedure is now presented. 1) Guess all unknown initial states and multipliers. 2) Converge an optimal trajectory containing no coast arc. However, monitor the switching function, $\Gamma(t)$, during this process. 3) If $\Gamma(t) > 0$ for the entire converged trajectory, no coast arc is required and the problem is solved. 4) If $\Gamma(t) < 0$ for some finite interval on the converged trajectory, choose values for T_0 and t_c [use the $\Gamma(t)$ plot as an aid]. 5) Converge an optimal trajectory containing the *specified* coast arc (i.e., fixed T_0 and t_c) using the converged values from step 2 as initial guesses for the unknown states and multipliers. Again monitor $\Gamma(t)$. 6) Shift the value of t_c until $|\Gamma(t_1) - \Gamma(t_2)| < \epsilon$ (a small number) Note that each shift of t_c will require reiteration of the optimization process (usually only one or two iterates are required). 7) Once a point on the Γ_{BAL} vs T_0 plot has been determined, change T_0 by a small amount. The relation

$$\delta t_i = \frac{-\alpha \Gamma_{BAL}(t_0)}{\Gamma(t_i)} \quad (i=1,2)$$

where $0 < \alpha < 1$, has been found to work well. 8) Repeat steps 5 and 6 using the converged initial states and multipliers from the last pass (step 6) as initial guesses. This will result in a second point on the Γ_{BAL} vs T_0 plot. 9) Extrapolate linearly to find the value of T_0 at which $\Gamma_{BAL}(T_0) = 0$. 10) Using the most recent initial conditions, the correct T_0, and the current value of t_c, repeat steps 5 and 6 to obtain the optimal trajectory. The result should give $\Gamma(t_1) = \Gamma(t_2) = 0$ upon reconvergence.

Numerical Example

The example problem studied was a low-thrust Earth-Jupiter transfer with one coast arc allowed but not required in the trajectory. Only the heliocentric phase of the mission was considered and only the solar gravitation was modeled (no drag, radiation pressure, etc.) All trajectories were assumed to leave Earth on the same day (November 15, 1983). The thrust level was full thrust or zero (no throttling).

The equations of motion for the vehicle are given by

$$\dot{x}_1 = -\frac{\mu}{r^3}x_4 + \frac{u_3 c}{x_7}\cos u_1 \cos u_2 \tag{1a}$$

$$\dot{x}_2 = -\frac{\mu}{r^3}x_5 + \frac{u_3 c}{x_7}\cos u_1 \sin u_2 \tag{1b}$$

$$\dot{x}_3 = -\frac{\mu}{r^3}x_6 + \frac{u_3 c}{x_7}\sin u_1 \tag{1c}$$

$$\dot{x}_4 = x_1 \qquad \dot{x}_5 = x_2 \tag{1d}$$

$$\dot{x}_6 = x_3 \qquad \dot{x}_7 = -u_3 \tag{1e}$$

where μ is the product of the universal gravitational constant, G, and the Sun's mass, r is the distance of the vehicle from the Sun, c is exhaust velocity of the low-thrust engine relative to the vehicle, x_1, x_2, x_3 are the vehicle's velocity components in

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*Associate Professor. Member AIAA.

†Engineer.