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SOLID PROPELLANT COMBUSTION MODELING

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Rockwell International Corporation

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## SOLID PROPELLANT COMBUSTION MODELING

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### ABSTRACT

This progress report covers the first 15 months of a continuing study on construction of a comprehensive mathematical model of composite solid propellant combustion, with emphasis on work during the past 12 months since reporting on the early efforts at the meeting last year.

The liquid layer believed to exist on burning ammonium perchlorate has been treated in a manner similar to that described last year. Depth of penetration of a thermal wave is calculated and this value is multiplied by the surface area of oxidizer on the burning propellant surface. The surface is calculated in the computer program for use in other equations. Total volume of the liquid layer derived in this manner is then used to calculate the thermal contribution to surface temperature.

Treatment of aluminum has been added, and the treatment of multimodal oxidizer has been improved. Most internal parameters have been thoroughly checked to verify that they have realistic values. Considerable time was spent on the Burke-Schumann flame height calculations. It has been found that at least seven terms of the series solution must be considered. The single first-term calculations that have been used in the past do not give a good assessment of flame height: the flame height is expressed implicitly in the final equation, and it was necessary to solve it by a Newton-Raphson iteration. Improvement in a number of input parameters is described. Gas phase conductivities were calculated using Chapman-Enskog theories with the Hirschfelder-Eucken corrector. The same theories were used to calculate diffusion coefficients. Stoichiometric ratios were calculated using more realistic pyrolysis species. A thermogravimetric analysis was made of a polybutadiene propellant binder and a statistical method was used to derive kinetic parameters from the thermograms. The method used was the Zsake modification of Doyle's method, which is probably the most sophisticated way of treating TGA data. Some other improvements in programming and correlation with actual propellant motor firings are shown and future plans are given.

### INTRODUCTION

Work continued during the past year on the comprehensive modeling of composite solid propellants.\* The model being developed is based on the Beckstead, Derr, Price multiflame model (1,2) and utilizes a critical particle size theory (5) to provide a means of calculating condensed phase heat release. A number of improvements have been made to the model and the computer program that was described at the meeting last year (4); one of

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the major improvements being the addition of a treatment of the liquid layer on burning ammonium perchlorate (AP). These improvements, an example experiment and future plans are described in the following paragraphs.

### MATHEMATICAL MODEL AND IMPROVEMENTS

The most recent surface energy balance is shown on Fig. 1. The new terms (not shown last year) are the energy to melt the aluminum and the energy from the liquid layer. In this equation  $m_{ox}$  is the mass flux of interstitial propellant; or, more specifically, the binder plus the subcritical AP. The term for condensed phase heat release based on the critical particle size theory is included. The critical particle size theory, stated simply, is that there exists for a given propellant and pressure a particle size where all smaller particles will be consumed in condensed phase reaction. The terms for aluminum fusion and liquid layer on AP are also present. The treatment of aluminum used is somewhat different from that used in the BDP model; with the methodology explained later.

|                                                        |                                                                                                                                       |                                          |                                            |                                   |
|--------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------|--------------------------------------------|-----------------------------------|
| ENERGY TO RAISE<br>PROPELLANT TO $T_s$                 | ENERGY TO VAPORIZE<br>OXIDIZER                                                                                                        | ENERGY TO VAPORIZE<br>FUEL               | ENERGY FROM<br>CONDENSED PHASE             | ENERGY<br>TO MELT AL              |
| $m_t c_p (T_s - T_0)$                                  | $- m_{ox} \frac{S_{ox}}{S_0} Q_L$                                                                                                     | $- (1 - \delta) m_p \frac{S_p}{S_0} Q_f$ | $+ \delta m_p \frac{S_p}{S_0} Q_s$         | $- m_{AL} \frac{S_p}{S_0} Q_{AL}$ |
| ENERGY FROM PRIMARY<br>DIFFUSION FLAME                 | ENERGY FROM AP FLAME                                                                                                                  | ENERGY FROM FINAL<br>DIFFUSION FLAME     | ENERGY FROM AP<br>LIQUID LAYER             |                                   |
| $+ \beta_t Q_{PF} m_t \exp \left( -\xi_{PF}^* \right)$ | $+ (1 - \beta_f) m_{ox} \frac{S_{ox}}{S_0} \left[ Q_{AP} \exp \left( \xi_{AP}^* \right) + Q_{FF} \exp \left( \xi_T^* \right) \right]$ |                                          | $+ \omega m_{ox} \frac{S_{ox}}{S} Q_{LIQ}$ |                                   |

Fig. 1. Critical Particle Size Model Energy Balance

Figure 2 shows first the current equation for surface temperature. This was derived from the energy equation using mass balance equations in the same manner as originally used by Beckstead (2). The next three equations are for the heat release in the primary, final, and AP flames.

**Flame Heights.** The Burke-Schumann equation modified for short flames is shown in Fig. 3. In the past a single term of this expression has been used but we have found that at least seven terms should be used. The equation is really not as complicated as it first appears; it is nothing more than is shown in the second equation. By adding the extra terms the equation has been made implicit in flame height but it is solved easily by a Newton-Raphson iteration. Convergence is obtained rapidly when the initial guess for flame height is taken as one-tenth the value obtained from a single-term calculation. This table is the numerical value of the first five terms; and each term is about half the value of the preceding term. An actual check of flame heights when different numbers of terms are used shows that at least seven terms must be used to get the flame within 1 micron.

SURFACE TEMPERATURE

$$T_s = T_o - \frac{\gamma}{C_p} Q_L - \frac{(1-\delta)(1-\gamma-\epsilon)}{C_p} Q_f + \frac{\delta(1-\gamma-\epsilon)}{C_p} Q_s + \epsilon Q_{AL} + \frac{\beta_F Q_{PF}}{C_p} \exp\left(-\xi_{PF}^*\right) +$$

$$(1-\beta_F) \frac{\gamma}{C_p} \left[ Q_{AP} \exp\left(-\xi_{AP}^*\right) + Q_{FF} \exp\left(-\xi_T^*\right) \right] + \frac{\omega \gamma}{C_p} Q_{L10}$$

HEAT RELEASE

$$Q_{PF} = C_p (T_f - T_o) + \gamma Q_L + (1-\delta)(1-\gamma-\epsilon) Q_f - \delta(1-\gamma-\epsilon) Q_s + \epsilon Q_{AL} - \omega \gamma Q_{L10}$$

$$Q_{FF} = \frac{C_p}{\gamma} \left[ (T_f - T_o) - \gamma(T_{AP} - T_o) \right] + \frac{(1-\delta)(1-\gamma-\epsilon)}{\gamma} Q_f - \frac{\delta(1-\gamma-\epsilon)}{\gamma} Q_s + \frac{\epsilon Q_{AL}}{\gamma} - \omega Q_{L10}$$

$$Q_{AP} = C_p (T_{AP} - T_o) + Q_L - \omega Q_{L10}$$

Fig. 2. Current Equations for Surface Temperature Used in Computer Program

FLAME HEIGHTS

$$\frac{\nu(1+\nu)C^2}{2(1+\nu)C} = \sum_{n=1}^{\infty} \frac{1}{\phi_n} \frac{J_1(C\phi_n)}{[J_0(\phi_n)]^2} \exp\left[-\frac{\left(1 + (2\psi\phi_n)^2\right)^{\frac{1}{2}} - 1}{2\psi^2} \eta\right]$$

$$A = B_1 \rho^{-C_1 \eta} + B_2 \rho^{-C_2 \eta} + \dots + B_n \rho^{-C_n \eta}$$

SIZE OF TERMS

|   |         |
|---|---------|
| 1 | - 0.072 |
| 2 | - 0.046 |
| 3 | - 0.024 |
| 4 | - 0.011 |
| 5 | - 0.005 |

SOLVED BY NEWTON-RAPHSON ITERATION

$$\eta_{n+1} = \eta_n - \frac{f(x)}{f'(x)}$$

Fig. 3. Burke-Schumann Equation Modified for Short Flames

A number of other improvements have been made to the computer program for this model. During the past year all parameters have been thoroughly checked, particularly those used internally and normally not listed. We found that some of the volume and weight fractions would become unrealistic; e.g., greater than one. When this occurred it caused discontinuities in the burn rate curve. This was remedied by setting boundaries on these parameters.

Treatment of the oxidizer particle size has been improved. The spline fit of the particle size distribution curve is still used. A normal bi- or tri-modal oxidizer blend will usually be split into 10 modes by this technique. Calculation of the  $h/D$  ratios is handled in a different manner than that described by Cohen, Derr, and Price last year (Fig. 4). Each mode of supercritical oxidizer is split into 50 parts; the ignition delay term in the equation for  $h/D$  is calculated for each part, summed and averaged. Each ignition term is then multiplied by the weight fraction of the mode and summed with similar terms produced from each mode. Then  $h/D$  and  $S_{ox}$  are calculated.

SURFACE DIMENSIONALITY

$$\frac{h}{D} = \frac{1}{2} \left( 1 \pm \frac{1}{\sqrt{3}} \right) \left( 1 - \frac{r_{ox}}{r_f} \right) + r_{ox} \frac{K_0 D^n}{p^m}$$

DIFFUSION COEFFICIENT

$$D_{AB} = \frac{C \sqrt{T^3 \left( \frac{1}{M_A} + \frac{1}{M_B} \right)}}{P \sigma_{AB}^2 \Omega_{AB}}$$

LIQUID LAYER TREATMENT

$$\omega = \frac{S_{ox}}{S} \frac{D_c}{l} \frac{\rho_{ox}}{\rho_p}$$

Fig. 4. Calculations for  $h/D$  Ratios

Oxidizer/fuel stoichiometric ratios are different in the primary flame and the final flame. At temperatures such as are found at the binder surface it is known that polybutadiene depolymerizes (5) with the major specie produced being butadiene. This is considered the major diffusing specie in the primary flame, giving a stoichiometric ratio of 3.7. The Chapman-Encog equation in the center of Fig. 4 was then used to calculate the diffusion coefficient for the primary flame. In the final flame it was assumed that hydrocarbon fragments were the major diffusing species; a stoichiometric ratio of 8.0 was used, along with a larger diffusion coefficient.

Liquid layer. The AP liquid layer was not treated as a melt but as an exothermic layer. We have always assumed this layer to be a solution of

AP and perchloric acid. A thermal wave penetration is calculated in the same manner as for the critical particle size. This volume is converted to weight fraction of AP in the propellant that is available for exothermic surface reaction (Ref equation at bottom of Fig. 4).

### EXPERIMENTAL RESULTS

The combustion model with the improvements noted above was applied to several smokeless propellants for which experimental data were available. Theoretical calculations for three of the propellants (based on carboxy-terminated polybutadiene binders) were made at two initial propellant temperatures and temperature sensitivities of burning rates were calculated. As shown in Table I, agreement of 77 F burn rates is good. Slopes of the burn rate curves are identical. The  $\sigma_k$  values were calculated using the one over one minus "n" relationship. The theoretical  $\sigma_k$  values are all low and should be two to three times higher; and we will look into this further.

Table I. Temperature Sensitivity

| EXPERIMENTAL  |       |            |            | THEORETICAL   |       |            |            |
|---------------|-------|------------|------------|---------------|-------|------------|------------|
| r at 1000 psi | SLOPE | $\sigma_p$ | $\sigma_k$ | r at 1000 psi | SLOPE | $\sigma_p$ | $\sigma_k$ |
| 0.43          | 0.38  | 0.10       | 0.16       | 0.38          | 0.36  | 0.04       | 0.06       |
| 0.29          | 0.50  | 0.07       | 0.13       | 0.27          | 0.50  | 0.02       | 0.05       |
| 0.45          | 0.50  | 0.10       | 0.21       | 0.40          | 0.50  | 0.03       | 0.07       |

Figure 5 shows a burning rate vs pressure plot; the upper line represents a least squares fit to rocket motor firings; the lower line, the theoretical. This is a two cycle-by-two cycle log-log plot. The scales are the same as those widely used in industry to plot rocket motor rate; therefore, the data are presented in a realistic, practical manner. As noted last year we did not use strand data for correlative purposes since strand rates are not necessarily predictive of motor rates. Propellant used in the motor from which the plotted data were taken has a Butarez CTL-type binder and an 86% solids loading. The trimodal oxidizer is comprised of commercial 200- and 80-micron fractions and Majac-ground

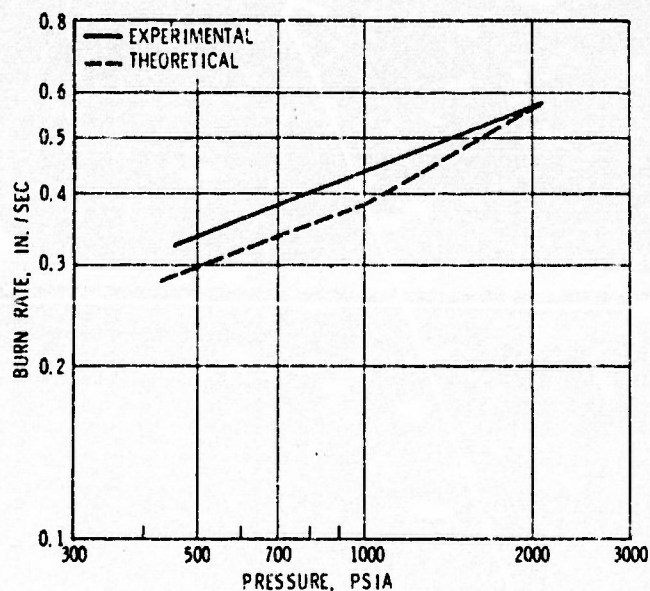


Fig. 5. Propellant with Butarez CTL Type with 86% Solids and Trimodal Oxidizer

10-micron AP at weight percent levels 55/26/25. The theoretical curve is identical in slope up to 1000 psi.

Comparable data with a propellant containing a trimodal mixture of 400-, 200-, and 80-micron AP at weight percent levels 51/20/15, respectively, are shown in Fig. 6. The break at 1000 psi is well verified by motor firings. No curve fitting was used to obtain these results; i.e., they were obtained on the first computer run. Fig. 7 shows data from a hydroxy-terminated polybutadiene (HTPB)-based propellant with a large amount of fine oxidizer; i.e., a trimodal blend of 200-, 80-, and 10-micron at weight percent levels of 31/15/40, respectively. Again, we are comparing motor data; and, although the burn rate is somewhat lower, the two lines have identical slopes. Data from a propellant that has a tetramodal oxidizer, i.e., 400-, 200-, 80-, and 10-micron at weight percent levels of 56/13/12/5, respectively, are shown in Fig. 8. We would like to emphasize again that no manipulation of parameters was required; the curve represents the first run made for the oxidizer blend with the current computer program.

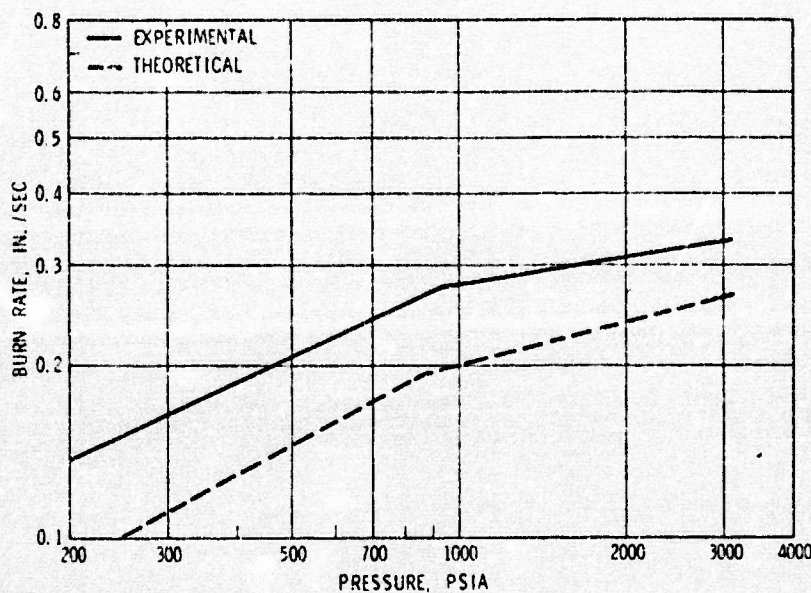


Fig. 6. Propellant with Butarez CTL Type Binder with 86% Solids and Trimodal Oxidizer

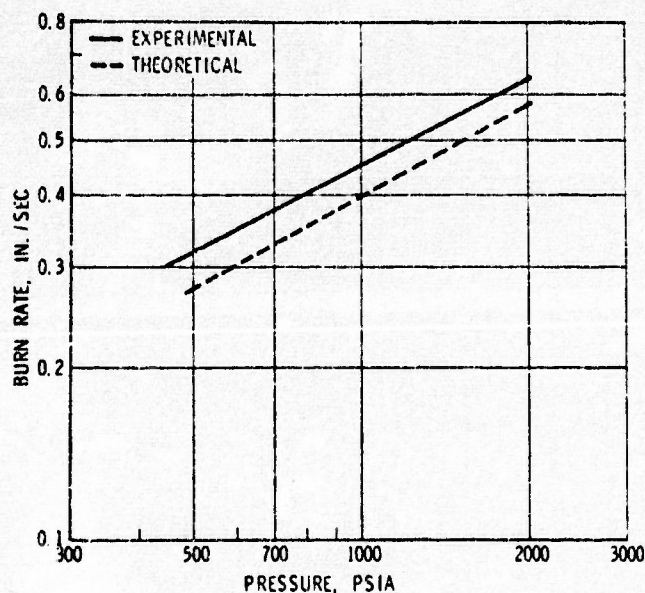


Fig. 7. Propellant with HTPB-Type Binder with 86% Solids and Trimodal Oxidizer

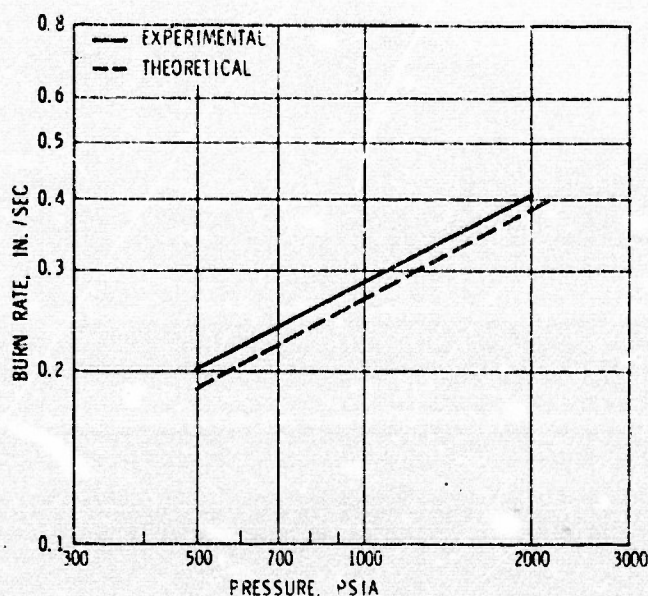


Fig. 8. Propellant with HTPB-Type Binder with 86% Solids and Trimodal Oxidizer

#### FUTURE PLANS

In the ensuing months, we plan to further study the possibilities of a two surface temperature model, add a treatment for the catalyst, and continue studying the effects of particle size. We will also establish possible maximum and minimum burn rates and continue to make improvements in the computer program.

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