Pressure dependence of catalysed and inhibited burning rate of composite solid propellants

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Data on ambient temperature burning rates for an aluminized HTPB composite propellant family with bimodal AP and a total solids loading of roughly 80% over the pressure range from 35 to 105 kg/cm² have been reported. Data are also reported for the additive free base line formulation and formulations with individual rate modifying additives (Fe₂O₃, copper oxide, CaCO₃, SrCO₃) at 2% level. Results have been correlated with rate expressions of Summerfield, Rice, Rastogi and several other empirical relations and relative merits of different equations have been assessed. Further, the experimental data of Blair on pressure and temperature dependence and of Singh on formulation dependence of burning rate have also been analysed. The results show that burning rate is directly proportional to (T)¹/₄, in agreement with the prediction based on burning rate expression of Rastogi et al. (T is the initial temperature in kelvin).

Understanding of the mechanism of catalysis and inhibition of burning rate of composite solid propellants is important from the viewpoint of solid-propellant rocket technology¹,². A knowledge of pressure dependence of burning rate in the presence of catalyst/inhibitor is also equally important. Phenomenon is know to be complex and technologists have mainly relied on empirical knowledge alone. Although several empirical relations between burning rate and pressure have been suggested¹-³, only a few have theoretical justification based on specific models. The recently suggested equation due to Rastogi et al.⁴, is based on a tubular reactor model which invokes the pressure dependence of some of the components of the combustion reactions. The model was clarified⁵ subsequently in response to the criticism of Nelson et al.⁶ The predictions of the model were found to be in agreement with experimental data for uncatalyzed propellants with erosive and non-erosive burning⁷ based on the data of King⁸ and Girdhar et al.⁹. The present investigation was undertaken to test whether the above model holds good for catalyzed/inhibited combustion of composite solid propellants and to interpret the results in terms of the model. Burning rate data at different initial temperatures¹⁰ and for different percentages of solids loading¹¹ have also been analysed.

Materials and Methods

Propellant formulations were made by casting technique using 99% pure ammonium perchlorate (AP) (WIMCO, Ambernath), Hydroxy terminated polybutadiene (HTPB) having viscosity of 5000 cp (25°C) (ARCO; R-45M, USA) and 99% pure aluminium (Al) (particle size 37 μ; Metal Powder Co., Madurai, India). Bimodal AP (50% coarse; 200 μ) and 50% fine (10 to 12 μ) was used. Emolein (diethyl-2-ethylhexylazelate) was used as a plasticizer. Ballistic modifiers (CaCO₃, SrCO₃, Fe₂O₃ and copper oxide, all BDH) of particle size 1.5 μ were used.

Propellant ingredients were mixed in a sigma Blade Incorporator for 2 hr and grain was cast in aluminium casting fixture (110 mm int. diam). Cast propellants were cured at 75°C for 8 days.

Burning rates at various pressures were determined employing Strand burner method (Crawford bomb). Propellants of 6 mm diameter were used for burning rate determination. Propellants (i) and (ii) had the compositions: (i) AP, 68%; HTPB, 20%; Al, 10%; and modifiers, 2%; and (ii) AP, 69.4%; HTPB, 20.4%; Al, 10.2%.

Results and Discussion

It is evident from the data in Table 1 that at all pressures the burning rate (r) for composite propellants is the highest for propellant containing copper oxide as modifier while it is the lowest for SrCO₃-containing propellant. Burning rate increases with increase in pressure in all the cases. The magnitude of effect of pressure on r is smaller in the case of propellants-
Table 1 — Burning rates of composite solid propellants (HTPB + AP + Al + modifiers) at different pressures.

<table>
<thead>
<tr>
<th>Modifier</th>
<th>Burning rate (mm/s) at pressures (kg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35</td>
</tr>
<tr>
<td>Nil</td>
<td>4.8</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>4.0</td>
</tr>
<tr>
<td>SrCO₃</td>
<td>3.7</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6.7</td>
</tr>
<tr>
<td>Copper oxide</td>
<td>11.5</td>
</tr>
</tbody>
</table>

containing the inhibitors such as SrCO₃ and CaCO₃ and higher in the case of propellants containing catalysts like copper oxide and Fe₂O₃. The experimental data have been analysed by least square method using Eqs (1-5).

\[
\frac{\dot{r}}{P} = \frac{a''}{P} - b''
\]  

\[
\ln \dot{r} = a^* + b^* \ln P
\]  

\[
P/\dot{r} = a_1 + b_1 P
\]  

\[
P/\dot{r} = a + b P^{2/3}
\]  

\[
\ln \dot{r} = m_1 P + c_1
\]

The constants of Eqs (1) and are given by Eqs (6) and (9).

\[
a'' = \frac{2 \lambda_2 (T_k - T_o) k_1 f_1(T)}{\left| T_1 - T_o \right| \ln (C_k / C_e)}
\]

\[
b'' = \frac{2 \lambda_2 (T_1 - T_o) k_2 \Delta V^m f_2(T)}{\left| T_1 - T_o \right| \ln (C_k / C_e)}
\]

The constants of Eqs (1) and are given by Eqs (6) and (9).

\[
a = \frac{\left[ \frac{1}{RT_k/M_k} \right] C_k (T_1 - T_o) - Q_k}{\left[ \lambda_k (T_1 - T_o) \right]^{1/2} A \exp \left( - E/RT_k \right)}
\]

It may be noted that Eqs (1) and (4) have theoretical basis (for significance of the terms, reference may be made to original papers4,12). The values of the constants of Eqs (1) to (5) along with correlation coefficients are given in Table 2. Figure 1 provides the graphical test of Eq. (1).

Table 2 — Correlation coefficients and constants of Eqs (1) to (5)

<table>
<thead>
<tr>
<th>Modifiers</th>
<th>Correlation coefficients</th>
<th>( h^* ) (mm/s)</th>
<th>( a^* ) (kg cm⁻²)</th>
<th>( a' ) (kg cm⁻² mm⁻³)</th>
<th>( c_1 ) (mm⁻¹)</th>
<th>( a'' ) (mm⁻¹)</th>
<th>( b^* ) (kg cm⁻³)</th>
<th>( b_1 ) (kg cm⁻³ mm⁻¹)</th>
<th>( b ) (kg cm⁻³ mm⁻¹)</th>
<th>( m_1 ) (kg⁻¹ cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nil</td>
<td>0.98 0.95 0.95 0.96 0.97 0.0023</td>
<td>0.02</td>
<td>4.80</td>
<td>1.89</td>
<td>1.32</td>
<td>0.72</td>
<td>0.43</td>
<td>0.09</td>
<td>0.55</td>
<td>0.007</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>0.99 0.99 1.00 1.00 1.00 0.0030</td>
<td>0.45</td>
<td>3.68</td>
<td>-1.21</td>
<td>1.25</td>
<td>0.55</td>
<td>0.26</td>
<td>0.16</td>
<td>0.93</td>
<td>0.004</td>
</tr>
<tr>
<td>SrCO₃</td>
<td>1.00 0.99 1.00 1.00 0.96 0.0028</td>
<td>0.64</td>
<td>2.70</td>
<td>-3.23</td>
<td>1.24</td>
<td>0.49</td>
<td>0.19</td>
<td>0.19</td>
<td>1.14</td>
<td>0.003</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.97 0.97 0.98 0.99 0.98 0.0044</td>
<td>0.39</td>
<td>3.28</td>
<td>1.15</td>
<td>1.66</td>
<td>1.36</td>
<td>0.41</td>
<td>0.07</td>
<td>0.40</td>
<td>0.007</td>
</tr>
<tr>
<td>Copper oxide</td>
<td>1.00 0.98 0.99 0.99 0.98 0.0020</td>
<td>1.33</td>
<td>1.47</td>
<td>-0.02</td>
<td>2.26</td>
<td>4.53</td>
<td>0.31</td>
<td>0.05</td>
<td>0.29</td>
<td>0.005</td>
</tr>
</tbody>
</table>
ther in terms of Eqs (1) and (4), in order to discriminate between the two equations. Perusal of data in Table 2 further shows that: (i) values of \( a'' \) are higher for propellant (HTPB + AP + Al) + catalyst than that for propellant without the catalyst; (ii) values of \( a'' \) for propellant + inhibitor are lower than that for propellant without the inhibitor; and (iii) values of \( b'' \) are higher for propellant + catalyst as compared to that for propellant + inhibitor. It is also clear from Table 2 that for the additives CaCO\(_3\), SrCO\(_3\) and copper ox-ide, \( a'' \) is negative and there is no order in the values of \( a \).

All the terms on the right hand side of Eqs (8) and (9), except \( \left[ C, (T - T_0) - Q_s \right]^{1/2} \) and \( \left[ \lambda_i (T_i - T) \right]^{1/2} \), are always positive. Following argument shows that \( \left[ C, (T - T_0) - Q_s \right]^{1/2} \) would always be positive. Following argument shows that \( \left[ C, (T - T_0) - Q_s \right]^{1/2} \) would also be positive. It is clear that, if \( C, (T - T_0) > Q_s \), both \( a \) and \( b \) would be positive. However, if \( C, (T - T_0) < Q_s \), both \( a \) and \( b \) would become imaginary since \( \left[ C, (T - T_0) - Q_s \right]^{1/2} \) would be negative. Hence, according to Eq. (4), both \( a \) and \( b \) should always be positive.

Blair\(^{10} \) has also mentioned that if the empirical values of \( a \) and \( b \) are to retain their physical meaning both \( a \) and \( b \) must be positive. On the other hand, in the case of Eq. (1) it is clear that both the constants \( a'' \) and \( b'' \) can be negative when \( C, (T - T_0) < Q_s \) [see Eqs (6) and (7)] or \( \Delta V^* \) is negative. From the above arguments, it follows that Eq. (4) does not fit the data for additives since \( a \) is negative contrary to the require-ment of the theory. On the other hand, there is no such inconsistency in the case of Eq. (1).

Eq. (7) suggests that \( b'' \) is related to \( \Delta V^* \). Now by definition, \( \Delta V^* \) = volume of activated complex-volume of reactants. Hence, \( \Delta V^* \) will have a larger value when a loose activated complex is formed while it will have a smaller value when tight complex is formed. The results suggest that volume of activation in the case of propellants containing catalysts is more due to formation of a loose activated complex as compared to the case of propellants without a catalyst or with an inhibitor. On the other hand, a tight activated complex is probably formed in the case of inhibitors on account of which \( \Delta V^* \) is small in comparison to catalyst.

Broadly speaking, the most probable chemical reactions which take place during the combustion of composite solid propellant are: (a) AP decomposition; (b) polymer degradation; (c) HClO\(_4\) decomposition; and (d) reaction of HClO\(_4\) or HClO\(_4\) decomposition products with polymer and polymer degradation products. The processes (a) to (d) have been studied separately by various workers\(^{13-16} \) and their results suggest that the combustion process of AP decomposition is the rate-determining. Therefore, \( \Delta V^* \) may be supposed to be related to AP decomposition. It is well established that AP decomposition takes place ac-cording to the sequence of reactions shown in Scheme 1\(^{17} \)

\[
\text{NH}_2\text{ClO}_4 \rightleftharpoons \text{NH}_3(a) + \text{HClO}_4(a) \rightarrow \text{Products}
\]

Sublimate \( \rightleftharpoons \text{NH}_3(g) + \text{HClO}_4(g) \rightarrow \text{Products}
\]

The primary step in AP decomposition is proton transfer process. However, it seems difficult to correl-ate \( \Delta V^* \) and \( b \), particularly in view of the fact that in-hibiting action also involves a change in the path of decomposition\(^{18} \) of complex since water and carbon dioxide are also released in the reaction between AP and inhibitor.

The values of \( a \) are related to the function \( f_i(T) \), which in turn is essentially a function of energy of activation which is smaller in the case of catalysts and larger in the case of inhibitors. Since, \( f_i(T) \) is a function of \( e^{-E/R T} \), it is obvious that \( f_i(T) \) would be larger for propellants containing catalysts and smaller for those containing inhibitors. Hence, the magnitude of \( a'' \) would be larger for propellants containing catalysts as compared to propellants without the catalysts. Similarly \( a'' \) would be smaller for propellants containing inhibitors in comparison to those without it. This is in accord with experimental data.

The effect of initial temperature (\( T_i \)) on the burning rate (\( \dot{r} \)) of composite solid propellant has been experi-mentially studied by Blair.\(^{10} \) The model of Rastogi et al.\(^3 \) suggests that both \( a'' \) and \( b'' \) are directly propor-tional to \( k_i \) [see Eqs (6) and (7)]. Since, \( k_i \) is the fre-quency factor and known to be directly proportional to square root of temperature\(^{19} \), we can write

\[
a'' = C_i T_i^{1/2}
\]

\[
b'' = C_2 T_i^{1/2}
\]

where \( C_i \) and \( C_2 \) are constants. Inserting the values of \( a'' \) and \( b'' \) from Eqs (10) and (11) in to Eq. (1), we get

\[
\left( \frac{\dot{r}}{P} \right)^2 = \frac{1}{P} \left( C_i T_i^{1/2} - C_2 T_i^{1/2} \right)
\]

At constant pressure Eq. (12) can be rewritten as

\[
(\dot{r})^2 = C_3 T_i^{1/2} - C_4 T_i^{1/2}
\]

where \( C_3 \) and \( C_4 \) are another set of constants. Therefore, according to Rastogi model \( a'' \) and \( b'' \) should be directly proportional to \( T_i^{1/2} \) and (\( \dot{r} \))^2 should be directly proportional to \( T_i^{1/2} \) at constant pressure.

Accordingly, the data of Blair was analysed using Eq. (1). The values of \( a'' \), \( b'' \), \( a''/b'' \) and correlation co-efficients are recorded in Table 3 and the plots of \( a'' \) and \( b'' \) against \( T_i^{1/2} \) are given in Figs 2 and 3, respectively. The values of \( \dot{r} \) for different initial temperatures at the same fixed pressure have been estimated from
Table 3—Correlation coefficients and constants* of Eq. 1

<table>
<thead>
<tr>
<th>Initial temperature (°C)</th>
<th>(a'') (in^2 s^{-2} \text{Psi}^{-1})</th>
<th>(b'') (in^2 s^{-2} \text{Psi}^{-2})</th>
<th>(a''/b'') (Psi)</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>89.4-94.4</td>
<td>(1.32 \times 10^{-4})</td>
<td>(-3.83 \times 10^{-9})</td>
<td>(-3.46 \times 10^{6})</td>
<td>0.998</td>
</tr>
<tr>
<td>35.5-44.4</td>
<td>(1.18 \times 10^{-4})</td>
<td>(1.81 \times 10^{-9})</td>
<td>(6.527 \times 10^{3})</td>
<td>0.999</td>
</tr>
<tr>
<td>1.1-3.3</td>
<td>(1.09 \times 10^{-4})</td>
<td>(3.28 \times 10^{-9})</td>
<td>(3.33 \times 10^{3})</td>
<td>0.999</td>
</tr>
<tr>
<td>-74.4-65</td>
<td>(0.90 \times 10^{-4})</td>
<td>(4.51 \times 10^{-9})</td>
<td>(2.00 \times 10^{3})</td>
<td>0.997</td>
</tr>
</tbody>
</table>

*For evaluation of constants the data have been taken from ref. 10.

Table 4—Correlation coefficients and constants* of Eqs (1), (3) and (4)

<table>
<thead>
<tr>
<th>Loading (%)</th>
<th>Eq.(1)</th>
<th>Eq.(4)</th>
<th>Eq.(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a'') (mm^2 s^{-2} kg^{-1} cm^2)</td>
<td>(b'') (mm^2 kg^{-1} cm^2 s^{-2})</td>
<td>(a''/b'') (kg cm^{-2})</td>
</tr>
<tr>
<td>80</td>
<td>0.60</td>
<td>1.53 \times 10^{-3}</td>
<td>0.39</td>
</tr>
<tr>
<td>82</td>
<td>0.72</td>
<td>1.68 \times 10^{-3}</td>
<td>0.43</td>
</tr>
<tr>
<td>84</td>
<td>0.94</td>
<td>2.29 \times 10^{-3}</td>
<td>0.41</td>
</tr>
<tr>
<td>86</td>
<td>1.34</td>
<td>4.22 \times 10^{-3}</td>
<td>0.32</td>
</tr>
<tr>
<td>88</td>
<td>1.92</td>
<td>7.08 \times 10^{-3}</td>
<td>0.27</td>
</tr>
</tbody>
</table>

*For evaluation of constants the data has been taken from ref. 11.

Fig. 2—Dependence of \(a''\) on initial temperature.

the plots of \((i/P)^2\) versus \(1/P\) drawn for different initial temperature. The plots of \((i)^2\) versus \(T_i^{1/2}\) at constant pressures are shown in Fig. 4. The linear plots obtained in Figs 2 and 4 show that \(a''\) is directly proportional to \(T_i^{1/2}\) and at constant pressure \((i)^2\) is directly proportional to \(T_i^{1/2}\) as predicted by the model proposed by Rastogi et al. The only weak point is that the linear dependence of \(b''\) on \(T_i^{1/2}\) is not clearly established (see Fig. 3), although it can not be taken as sufficient ground for rejection of the model. From Eqs (6) and (7) it follows that:

\[
a''/b'' = \frac{1}{\Delta V} \frac{f_i(T)}{f_2(T)}
\]

(14)

It should be noted that \(a''/b''\) is not independent of initial temperature since both \(T_i\) and \(T_f\) would depend on initial temperature and the functional dependence of \(f_i(T)\) on \(T_i\) and \(f_2(T)\) on \(T_i\) is not the same.
The burning rate data\textsuperscript{11} for aluminized AP/HTPB having different percentages of solid loading at different pressure and ambient temperature was smoothed and then analysed in terms of Eqs (1), (3) and (4). The correlation coefficients along with the constants of these equations recorded in Table 4, show that all the equations fit the data equally well. The values of $a''$, $a$, $a_1$; $b''$, $b$, $b_1$; $a''/b''$, $a/b$ and $a_1/b_1$ are plotted against solids loading percentages in Figs 5-7. The data appear to fit smoothly. However, the data could not be analysed further in view of the difficulty in estimating the various parameters in Eqs (1) and (4).
Acknowledgement

The authors thank the Ministry of Defence for supporting the investigation.

Abbreviations

\( \dot{r} \) = burning rate  
\( P \) = pressure  
\( \lambda_{sp} \) = average thermal conductivity of flame gas at the surface  
\( T_{fr} \) = flame temperature at the end of the chemical reaction zone  
\( T_s \) = surface temperature of the burning propellant (average)  
\( l_p \) = propellant density  
\( R \) = gas constant  
\( \Delta V^* \) = volume of activation i.e. difference in the volume of activated complex and the reactants.  
\( f_1(T) = T_s \exp \left( - \frac{E}{RT_s} \right) - T \exp \left( - \frac{E}{RT} \right) \) 
\( f_2(T) = \ln T_s \exp \left( - \frac{E}{RT_s} \right) - \ln T \exp \left( - \frac{E}{RT} \right) \) 
\( C_s \) = specific heat of solid (average of fuel and oxidizer)  
\( C_{eq} \) = equilibrium concentration of fuel species \( f \) at the end of chemical reaction zone  
\( C_{fa} \) = concentration of species \( f \) near the propellant surface  
\( Q_n \) = net heat release (+ ve) for gasification of the propellant  
\( T_0 \) = ambient temperature  
\( k_s \) = frequency factor  
\( AP \) = ammonium perchlorate  
\( HTPB \) = Hydroxy terminated polybutadiene

References