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Initial Temperature and Pressure Effects on Composite Solid-Propellant Burning Rates: Comparisons with Theory

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Pressure vs burning rate data are presented for an ammonium perchlorate composite solid propellant at four levels of initial temperature. For each level of initial temperature the data are fitted by least squares to the equation $P/r = a + bP^N$. Three values of N are considered at each temperature level, $N = 1$, $N = \frac{2}{3}$ and N = value for best fit to the data. These fits are then used to evaluate the relative merits of two burning rate laws, $N = 1.00$ corresponding to a law that includes the axisymmetric jet diffusion flame theory and $N = \frac{2}{3}$ corresponding to the Summerfield granular diffusion flame theory. The relative variation of the parameters a and b with temperature is compared with the expectation of the Summerfield theory. It is concluded that although $N = \frac{2}{3}$ gives a superior fit to $N = 1.00$, no law of the type $P/r = a + bP^N$ fits the data without systematic error and that the variation of best fit N with initial temperature casts doubt upon the physical model underlying both burning rate laws. The burning rate law suggested by Fenn, $P/r = a + brP^N$ also is tested. Its best fit is superior to that for $N = 1$ in the previous equation but it is inferior to the fit of that law for $N = \frac{2}{3}$ or N taken as the best fit value.

Nomenclature

a = gas phase reaction time parameter or first adjustable parameter
A = Arrhenius prefactor
b = diffusion time parameter or second adjustable parameter
C_s = specific heat of solid propellant
D = gas phase binary diffusion coefficient
E = activation energy
M_g = average molecular weight of the gas phase
N = pressure index in equation for P/r
P = absolute pressure, psia in data
Q_s = heat released in the solid phase
R = gas constant per mole
r = burning rate, in./sec in data
T_g = effective absolute temperature of the combusting gases
T_o = initial absolute temperature of the solid propellant (this is given as °F in the data but it appears always in the theories as degrees absolute)

T_s = absolute temperature of the burning surface of the solid propellant
T_1 = absolute temperature of the flame
ρ_s = density of the solid propellant
λ_g = thermal conductivity of the gas phase at the solid surface
μ = average oxidizer particle size

Introduction

PERHAPS the most successful theory of the steady-state burning rates of ammonium perchlorate composite solid-propellants is the granular diffusion flame theory of Summerfield.[1] It is a rather intuitive theory based upon a plausible model of the propellant gas phase flame structure, the details of which are extremely resistant to precise experimental investigation. Because the assumed flame structure has not been definitively investigated experimentally, the principal verification of the theory rests upon its agreement with such readily determined propellant characteristics as the variation of burning rates with pressure and with oxidizer particle size and particle size distribution. With regard to the effects of pressure the theory is quite explicit. This dependence is given as

$$1/r = (a/P) + b/P^{1/3} \qquad (1)$$

The constants a, the "gas-phase reaction time parameter," and b, the "diffusion time parameter," although independent of pressure are functions of other physical variables, including temperature, as will be discussed later. Equation (1) is formed by assuming that the gas phase flame zone thickness

Table 1   Least squares fit of P/r to various burning rate laws for temperature range 193°F to 202°F

P, psia	r, in./sec	P/r	Laws of class $P/r = a + bP^N$		Law of class $P/r = a + brP^N$	
					Best fit	Best fit
			$N = 1.00$	$N = \frac{2}{3}$	$N = 0.585$	$N = 0.18$
31.0	0.0635	488	29.7	8.1	−0.6	2.7
30.6	0.0638	480	30.9	9.4	0.6	4.5
68.0	0.1015	670	13.7	4.9	3.0	5.4
69.5	0.0975	713	8.6	−0.2	−2.1	−2.9
128.2	0.136	943	−3.6	−1.5	−0.1	−0.7
128.2	0.136	943	−3.6	−1.5	−0.1	−0.7
201	0.171	1175	−9.9	−1.7	0.7	0.5
203	0.174	1167	−8.6	−0.5	1.9	2.8
420	0.230	1826	−17.6	−6.7	−4.2	−8.7
416	0.234	1778	−15.2	−4.5	−2.0	−4.5
819	0.3325	2463	−1.3	1.9	2.4	4.3
815	0.3335	2444	−0.9	2.4	2.9	5.2
1203	0.3815	3153	3.7	0.3	−0.8	−1.4
1203	0.3805	3162	3.4	0.0	−1.0	−1.9
1590	0.3785	4201	Not included in fits			
1590	0.378	4344	Not included in fits			
$a =$			627.1	280.1	132.97	256.299
$b =$			2.201	25.49	47.24	2085.16
Standard deviation of residuals =			143.16	47.86	37.09	69.98
Index of determination =			0.975467	0.997259	0.998354	0.994138

is a linear combination of a chemical reaction length that is inversely proportional to the pressure and a diffusion length that is inversely proportional to the pressure to the one-third power. Thus, in Eq. (1) the term a/P represents the chemical kinetics of the process, whereas the term $b/P^{1/3}$ represents the "granular diffusion flame." If one uses the axisymmetric jet diffusion flame model of Rice[2] in this same theory the result is to remove the pressure dependence in the second term of Eq. (1) to give

$$1/r = (a/P) + b \qquad (2)$$

In Eq. (2) a and b are again two pressure independent constants. Equations (1) and (2) are thus two similar results for a single theory of solid-propellant burning rates wherein the assumption of a three-dimensional granular diffusion flame structure produces Eq. (1) and the assumption of an axisymmetric jet diffusion flame structure leads to Eq. (2). Both assumptions regarding the diffusion flame structure result in a pressure dependence for the burning rate when combined with the chemical kinetic term in a manner consistent with the Summerfield theory.

Both diffusion flame structures are plausible. Equations (1) and (2) offer the possibility of evaluating the two theories through examining burning rate vs pressure behavior. This behavior, although not a sensitive test of either theory, certainly may provide a relative evaluation of them.

In Ref. 3 some rather explicit expressions are presented regarding the parameters a and b in Eq. (1). They are

$$a \cong [\rho_s R T_g / M_g][C_s(T_s - T_o) - Q_s]^{1/2} \times$$
$$[\lambda_g(T_1 - T_s)]^{-1/2}[A \exp(-E/RT_g)]^{-1} \qquad (3)$$

$$b \cong \mu^{1/3}\rho_s[RT_g/M_g]^{5/6}[C_s(T_s - T_o) - Q_s]^{1/2} \times$$
$$[\lambda_g(T_1 - T_s)]^{-1/2}[PD_g]^{-1/2} \qquad (4)$$

In Eq. (4) the product of the pressure and the binary gas phase diffusion coefficient PD_g, is pressure independent.

Equations (3) and (4) offer additional tests of the physical model proposed by Summerfield. An investigation of the effects of particle size on the empirically determined constants a and b is one such test that was reported in the work of Bastress.[4] Another test is to determine the relative effects

of temperature upon the constants a and b obtained from empirical fits of Eq. (1) to burning rate vs pressure data.

If one takes the ratio of b to a as given by Eqs. (3) and (4) and if one assumes that $D_g \propto T^{1.5}$ one gets the following expression:

$$b/a = KT_g^{-11/12} \exp[-E/RT_g] \qquad (5)$$

In Eq. (5) the constant K is a combined constant that is independent of temperature.

Differentiating Eq. (5) with respect to T_g yields

$$d(b/a)/dT_g = (b/a)[(E/RT_g^2) - (11/12T_g)] \qquad (6)$$

If the empirical values of a and b are to retain their physical meaning both a and b must be positive. Thus, in any physically meaningful situation all terms on the right-hand side of Eq. (6) are positive and the sign of $d(b/a)dT_g$ depends upon the relative magnitudes of E/RT_g^2 and $11/(12T_g)$. Only if $E/RT_g < 11/12$ can $d(b/a)/dT_g$ be negative.

In the experimental work that is the subject of this communication a series of burning rate vs pressure curves were generated for an ammonium perchlorate composite solid-propellant with initial temperature as a parameter. The investigation considered the relative merits of Eqs. (1) and (2) on the basis of best least square fits to the experimental data and a determination of the sign of $d(b/a)/dT_g$ for Eq. (1). For the propellants used T_g was of the order of 2800°K. From the previous discussion this requires that $d(b/a)/dT_g > 0$ when $E > 5.1$ kcal/mole. Inasmuch as E is expected to be considerably above this value for typical hydrocarbon flames, the Summerfield theory leads to the expectation that b/a increases with T_g for the propellants tested. This test assumes that T_g varies monotonically with T_o.

Experimental Results

Burning rate vs pressure data were taken on uninhibited $\frac{1}{4}$-in.-diam. strands of 80% ammonium perchlorate/20% styrene base polyester resin propellant. The oxidizer was a bimodal blend of 70% unground-mean particle size 200 μ- and 30% ground-mean particle size 25 μ-ammonium perchlorate. Calculated on a weight average basis this gives

Table 2 Least squares fit of P/r to various burning rate laws for temperature range 96°F to 112°F

| | | | Percent error for various fits | | | |
| | | | Laws of class $P/r = a + bP^N$ | | Law of class $P/r = a + brP^N$ | |
P, psia	r, in./sec	P/r	$N = 1.00$	$N = \frac{2}{3}$	Best fit $N = 0.605$	Best fit $N = 0.22$
29.2	0.0574	509	26.2	4.9	−1.0	1.9
28.4	0.0574	495	28.0	6.6	0.5	4.3
29.0	0.0588	493	28.4	7.5	1.7	5.9
31.0	0.0620	500	28.0	8.4	3.2	7.7
67.7	0.0928	730	7.7	2.2	1.8	3.1
68.9	0.0905	761	4.0	−1.2	−1.5	−2.4
130	0.1278	1017	−6.6	−0.2	1.6	1.9
129	0.1248	1034	−8.7	−2.2	−0.3	−1.4
215	0.1539	1397	−18.8	−6.0	−3.4	−7.2
212	0.1567	1353	−15.8	−3.4	−0.9	−2.6
425	0.213	1995	−15.7	−3.4	−1.3	−3.3
420	0.2095	2005	−17.1	−4.6	−2.5	−5.6
814	0.2985	2727	0.5	3.8	4.2	7.6
811	0.294	2759	−0.9	2.5	2.9	5.2
1200	0.3315	3620	3.4	−0.5	−1.5	−2.9
1202	0.3325	3615	3.7	−0.3	−1.3	−2.5
1594	0.3205	4973	Not included in fits			
1591	0.323	4926	Not included in fits			
$a =$			613.6	254.0	142.2	270.514
$b =$			2.614	29.63	46.91	2057.33
Standard deviation of residuals =			166.3	53.18	45.67	87.96
Index of determination =			0.975585	0.997503	0.998158	0.993169

a mean particle diameter of 147 μ. This propellant conforms to conditions within the range of validity that is claimed for the Summerfield theory.[6]

The propellant was burned over a pressure range from 25 to 1600 psia in a purged strand burner. An upward flow of nitrogen, conditioned to the specified initial temperature, about the downward burning strands resulted in flat burning surfaces normal to the strand axes and in unusually low scatter in the data.

Four ranges of initial temperature were studied; 193°F to 202°F, 96°F to 112°F, 34°F to 38°F, and −103°F to −85°F. These ranges represent the scatter in the initial temperature at the given level about the mean initial temperature intended.

Over the lowest temperature range the propellant would not burn below 100 psia nor at 1600 psia. In one case a strand also extinguished at 1200 psia.

The data were fitted by least squares to laws of the

Table 3 Least squares fit of P/r to various burning rate laws for temperature range 34°F to 38°F

| | | | Percent error for various fits | | | |
| | | | Laws of class $P/r = a + bP^N$ | | Law of class $P/r = a + brP^N$ | |
P, psia	r, in./sec	P/r	$N = 1.00$	$N = \frac{2}{3}$	Best fit $N = 0.605$	Best fit $N = 0.26$
31.3	0.0579	541	33.7	6.8	0.3	6.1
31.0	0.0579	535	34.3	7.3	0.8	6.9
69.2	0.0879	787	14.7	2.9	1.3	3.5
70.0	0.0876	799	13.7	2.0	0.4	2.0
128.2	0.1168	1098	−0.5	0.0	0.6	0.6
128.2	0.1172	1094	−0.2	0.3	0.9	1.2
212	0.1431	1483	−11.4	−3.2	−1.7	−4.0
213	0.1431	1490	−11.7	−3.4	−1.9	−4.4
418	0.196	2133	−11.3	−0.7	0.6	0.2
419	0.189	2217	−15.5	−4.6	−3.1	−6.9
415	0.191	2173	−13.9	−3.1	−1.6	−4.0
810	0.264	3068	−1.2	2.6	3.0	5.3
811	0.266	3049	−0.4	3.3	3.6	6.6
1208	0.293	4123	0.9	−2.1	−2.7	−5.1
1202	0.300	4007	3.3	0.4	−0.1	0.0
1205	0.301	4003	3.6	0.6	0.1	0.3
1592	0.310	5135	Not included in fits			
1595	0.284	5616	Not included in fits			
1590	0.291	5464	Not included in fits			
$a =$			726.8	248.4	140.36	299.149
$b =$			2.845	33.41	47.56	1953.76
Standard deviation of residuals =			174.7	55.49	51.52	98.86
Index of determination =			0.979829	0.997965	0.998246	0.993541

Table 4   Least squares fit of P/r to various burning rate laws for temperature range $-102°F$ to $-85°F$

			Percent error for various fits			
			Laws of class $P/r = a + bP^N$		Law of class $P/r = a + brP^N$	
P, psia	r, in./sec	P/r	$N = 1.00$	$N = \frac{2}{3}$	Best fit $N = 0.86$	Best fit $N = 0.78$
128.5	0.1041	1234	9.8	−2.8	5.0	12.7
130.0	0.1071	1214	11.6	−0.4	7.0	14.8
217.5	0.1332	1633	2.3	1.0	1.5	3.1
250	0.1390	1799	−0.8	0.0	−0.7	−1.1
243	0.1307	1859	−5.7	−5.2	−5.7	−7.7
419	0.1710	2450	−3.9	1.2	−1.8	−5.2
420	0.1645	2553	−8.1	−2.7	−5.9	−11.7
420	0.1652	2542	−7.6	−2.2	−5.4	−11.0
821	0.228	3601	3.3	5.5	4.3	6.1
825	0.2325	3548	5.1	7.2	6.0	9.0
835	0.2215	3770	0.0	2.2	1.0	0.6
1205	0.238	5063	−0.6	−3.6	−1.7	−2.4
1205	0.2375	5074	−0.8	−3.8	−1.9	−2.7
$a =$			931.7	130.5	671.89	1123.13
$b =$			3.403	42.00	9.642	63.4476
Standard deviation of residuals =			120.5	128.2	112.0	189.0
Index of determination =			0.990968	0.989769	0.992202	0.977788

form

$$p/r = a + bP^N \qquad (7)$$

For Summerfield's Eq. (1), N has the value $\frac{2}{3}$ whereas for Eq. (2), which incorporates Rice's model, N has the value unity.

Best fits were obtained using a and b as adjustable constants for the previous two values of N and an additional fit was made where N also was taken as an adjustable constant. In calculating the least squares fits, data taken around 1600 psia were ignored. At this pressure the value of r showed a slight decrease with increasing pressure. This was systematically contrary to possible fits of Eqs. (1) and (2) and data in this range were omitted to avoid biasing the results at lower pressures which appeared to be at least roughly consistent with these equations. The burning rate law recently proposed by Fenn,[5] $P/r = a + brP^N$, also was fit to these data using a best fit value of N. The results are shown in Tables 1–6. Errors and deviations refer to $(P/r)_{fit} - (P/r)_{data}$.

The index of determination shown in these tables is a measure of the goodness of the fit. It has a limiting value of unity and it approaches that value as the fit is improved.

Tables 1–4 show a clear systematic deviation from fits with $N = 1.00$ or $\frac{2}{3}$ for the equation $P/r = a + bP^N$. The fit for $N = \frac{2}{3}$ is significantly better than for $N = 1.00$, with the improvement being greatest, in terms of percent error, at the lowest pressures. The Summerfield law appears to be definitely superior to the law based on the Rice model, but it is important to remember that both laws show a definite systematic error and that neither law can represent the data from 1200 to 1600 psia. The Fenn equation gives fits generally better than those of the Rice model and poorer than those of the Summerfield model over the pressure range fit to the equations except over the lowest temperature range. There the Fenn equation gives the least satisfactory fit.

In the particular case of the Summerfield law, the ratio b/a decreases with increasing temperature—see Table 6—in direct contradiction to its expected behavior. The best fit value of N is seen from Table 6 to increase steadily with decreasing temperature. The change is quite sharp going from the range around 34°F to that around −90°F. This region of sharp change may in part reflect the lack of low-pressure data points for the lowest temperature range. The extinction phenomena encountered in the lowest temperature range are not predicted by either theory. Modified theories that include heat loss terms would be expected to predict such phenomena.

For the best fit N, the behavior of b/a as a function of T_o is rather indefinite. The general trend appears to be for this ratio to increase with increasing T_o as we would expect if we retain the Summerfield interpretation of the physical significance of a and b.

For the Fenn equation the best fit value of N increases with decreasing initial temperature. The increase is gradual going from 200°F to 34°F but it is very sharp going from 34°F to −90°F.

Conclusions

1) The equation based upon the granular diffusion flame theory more closely represents the data than do equations based upon the axisymmetric jet diffusion flame theory or upon the Fenn theory. However, all three equations show

Table 5 a, b, and b/a for $N = \frac{2}{3}$ as functions of temperature

Range of T_o, °F	a	b	b/a
193 to 202	280.1	25.49	0.091
96 to 112	254.0	29.63	0.117
34 to 38	248.4	33.41	0.135
−102 to −85	130.5	42.00	0.322

Table 6   Best fit N with a and b as a function of temperature for $P/r = a + bP^N$

Range of T_o, °F	N	a	b	b/a
193 to 202	0.585	133.0	47.25	0.356
96 to 112	0.605	142.2	46.91	0.330
34 to 38	0.62	115.1	51.32	0.446
−102 to −85	0.86	754.5	7.149	0.00947

a clear systematic variation about the data points. Using best fit values of N significantly reduces the systematic deviation for the Summerfield type equation but it does not eliminate it. None of the equations tested represents the data within the limits of the random variation of the data points.

2) Laws of the form $P/r = a + bP^N$ fit to the data below 1200 psia are inconsistent with the behavior of the data above 1200 psia. The Fenn equation also suffers from this shortcoming.

3) The behavior of the ratio b/a with increasing temperature appears to be inconsistent with the physical interpretation of these terms in the Summerfield theory.

4) The best fit value of N is a function of temperature. This is in contradiction to the theories discussed in the preceding sections and it raises serious doubts regarding the adequacy of the physical models underlying these theories.

5) As the initial temperature is lowered, both high- and low-pressure limits of deflagration appear. The existence of these limits requires modification of the previous theories if it is to be explained. A theory that incorporates heat losses will give rise to deflagration limits, although the limits observed may not be caused primarily by heat losses.

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