Aluminized and Non-Aluminized AP/HTPB-Composite Propellant Burning Rates at Very-High Pressures

Catherine A. M. Dillier, Thomas Sammet, Felix A. Rodriguez, Erica D. Petersen, James C. Thomas and Eric L. Petersen
J. Mike Walker ’66 Department of Mechanical Engineering, Texas A&M University
College Station, Texas, USA

1 Introduction

Solid propellants are composed of either homogeneous or heterogeneous mixtures of fuel and oxidizer. Composite solid propellants can be tailored, particularly the burning rate, for specific applications through the inclusion of additives or by modifying the oxidizer average particle size. Over a limited range of pressures, the burning rate for ammonium perchlorate (AP)-based solid propellants is often described by the Saint Robert-Vielle law, Eqn. 1, where r is the burning rate, P the pressure, and a and n are experimentally determined coefficients. This burning rate-pressure relationship begins to break down however at very high pressures when the pressure exponent, n, drastically increases and the burning rate exhibits a “slope break” or “exponent break”, as referred to henceforth in the current study. This exponent break occurs at some characteristic pressure, P^*, which typically lies above 14 MPa (2000 psi) for AP-based propellants [1].

$$r = aP^n \tag{1}$$

As shown in Table 1, very-high-pressure testing has been conducted before [1-8]. Most of these studies however investigated the deflagration characteristics of pure AP only. While additional high-pressure studies with AP-based propellants have been performed in government research laboratories, Table 1 demonstrates the limited amount of burning rate data available for composite AP/HTPB-based propellants in the open literature. Many strand burner facilities are capable of determining composite propellant burning rates, but most of these only test regularly up to about 15.5 MPa (2250 psi). Few burning rate data exist for higher pressures and almost none for pressures exceeding 34.5 MPa (5000 psi). As a result, most studies fail to capture the exponent break phenomenon. Therefore, the objective of this study was to expand the burning rate pressure range for aluminized and non-aluminized AP/HTPB-composite propellants up to 68.9 MPa (10,000 psi). This paper presents the results of these new data, with emphasis on ballistic curve exponent changes at these extreme pressures.

Correspondence to: cdillier2301@tamu.edu

Table 1. Brief survey of previous high-pressure studies utilizing pure AP or AP-based composite propellants [1-8].

Study	Propellant Type	Maximum Pressure Tested
Friedman & Nugent (1955)	Pressed AP Pellets	~50 MPa (7250 psi)
Levy & Friedman (1962)	Pressed AP Pellets (asbestos wrapped)	~41.4 MPa (6000 psi)
Glaskova (1963)	Pressed AP Pellets	~100 MPa (14,500 psi)
Irwin, et. Al. (1963)	Pressed AP Pellets (plioband inhibited, asbestos wrapped)	~158.6 MPa (23,000 psi)
Bobolev et. Al. (1964)	Pressed AP Pellets (clear)	~68.9 (10,000 psi)
Boggs (1970)	Single AP Crystals	~41.4 MPa (6000 psi)
Kanelbaum et. Al. (2011)	AP/HTPB-based composite propellant grains with Fe_2O_3 and silicone carbide	~58.6 MPa (8500 psi)
Atwood et. Al. (2013)	AP/HTPB- based composite propellants containing various AP particle sizes, μm-Al, Fe_2O_3, and Dioctyl Adipate (DOA) or Dioctyl Sebacate (DOS) plasticizers	~345 MPa (50,000 psi)

2 Methods

In this study, four non-aluminized and aluminized composite propellant formulations were tested up to 68.9 MPa (10,000 psi). Each formulation contained ammonium perchlorate (AP) as the oxidizer; R45-M hydroxyl-terminated polybutadiene (HTPB), the fuel-binder; and isophorone diisocyanate (IPDI), the curative. As seen in Table 2, two of the formulations were baselines with no additive, and the other two were aluminized. The baselines had 80 and 85% solids loadings with monomodal and bimodal AP distributions, respectively. An average particle size of 200 μm was used in the monomodal propellants, and a 70:30 200-to-20-μm (coarse-to-fine) AP ratio was used in the bimodal formulation. Both of the aluminized mixtures contained a monomodal AP distribution with 24-μm aluminum from Firefox Enterprises LLC at mass percentages of 8% and 16%. Techniques developed by Stephens et al. were used to produce all of the propellants in the authors' laboratory [9]. Table 2 provides the detailed formulation matrix used in this study.

A minimum of ten, 25.4-mm-long and 4.76-mm-diameter propellant samples were burned for each formulation in two, constant-volume pressure vessels using nichrome wire ignition. Pressures up to 34.5 MPa were tested in the authors' high-pressure facility as described by Carro et al. and Kreitz et al. [10-11]. To test the higher pressures up to 68.9 MPa, a new very-high pressure strand burner facility was recently developed and characterized at Texas A&M University as described by Dillier et al. [12]. Both vessels were pressurized using inert nitrogen gas, with pressures above 34.5 MPa achieved using an air-supplied Haskel AG-75 gas booster. Fitted burning rate trends for each formulation in the form of $r = aP^n$ with r the burning rate (mm/s), P the pressure (MPa), and a and n experimental constants, are provided in Table 2.

Table 2. Propellant compositions and respective burning rate information evaluated in the current study.

Solids Loading (Mass %)	AP Distribution	Al Mass %	Characteristic Pressure, P^*	Below P^*			Above P^*		
				Average Burning Rate Below P^* (mm/s)	Burning Rate Coefficients		Average Burning Rate Above P^* (mm/s)	Burning Rate Coefficients	
					a	n		a	n
80	Monomodal	-	36.5 MPa (5300 psi)	9.70	2.480	0.60	40.24	0.133	1.44
85	Bimodal	-	25.8 MPa (5200 psi)	10.91	2.769	0.60	46.24	0.144	1.46
83	Monomodal	8.00	28.9 MPa (4200 psi)	10.02	2.772	0.56	40.55	0.070	1.64
83	Monomodal	16.00	29.6 MPa (4300 psi)	9.64	2.158	0.65	33.53	0.181	1.32

3 Results and Discussion

The non-aluminized baseline propellant burning rate results are plotted in Fig. 1. The exponent break is evident for both formulations. Both baselines have a characteristic pressure, P*, slightly above 34.5 MPa (5000 psi). The 80% monomodal baseline characteristic pressure is slightly higher than that of the 85% bimodal. However, they are extremely close, 36.5 MPa (5300 psi) compared to 35.8 MPa (5200 psi), so further investigation is required to determine whether or not the AP size distribution significantly affects the characteristic pressure. The pressure exponents for both baselines were also extremely close at 1.44 and 1.46. It is important to note that testing above 34.5 MPa (5000 psi) was required to determine the characteristic pressure, further emphasizing the need for obtaining very-high-pressure burning rates like those in the present study.

Figure 2 presents the burning rate results for both aluminized propellant formulations. Again, the exponent break is noticeably evident for both formulations, and testing above 34.5 MPa (5000 psi) was required to establish the characteristic pressure. Similar to the AP distribution for the baseline formulations, the aluminum concentration does not appear to significantly affect the characteristic pressure. It does however, lower the characteristic pressure compared to the baselines from slightly above 34.5 MPa (5000 psi) to 28.9 MPa (4200 psi) and 29.6 MPa (4300 psi) for the 8% and 16% aluminized mixtures, respectively. Furthermore, while the baselines exhibited similar pressure exponents, the aluminized propellants did not. The doubling in aluminum mass percentage from 8% to 16% decreased the pressure exponent from 1.64 to 1.32. However, this decrease in exponent value could be attributed to uncertainty in the data analysis, and further investigation is required.

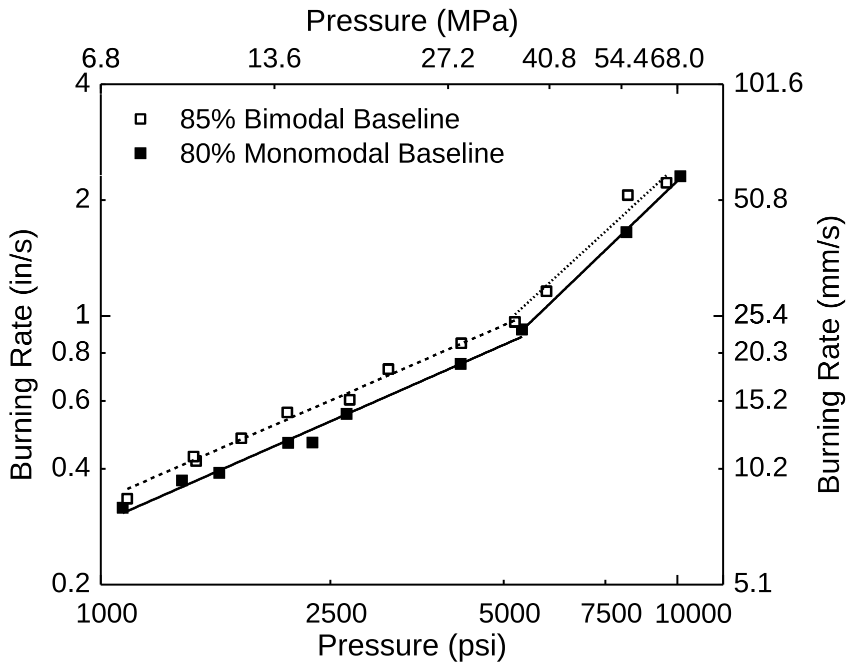

Figure 1. High-pressure burning rate results for 80% monomodal and 85% bimodal baselines with no additives.

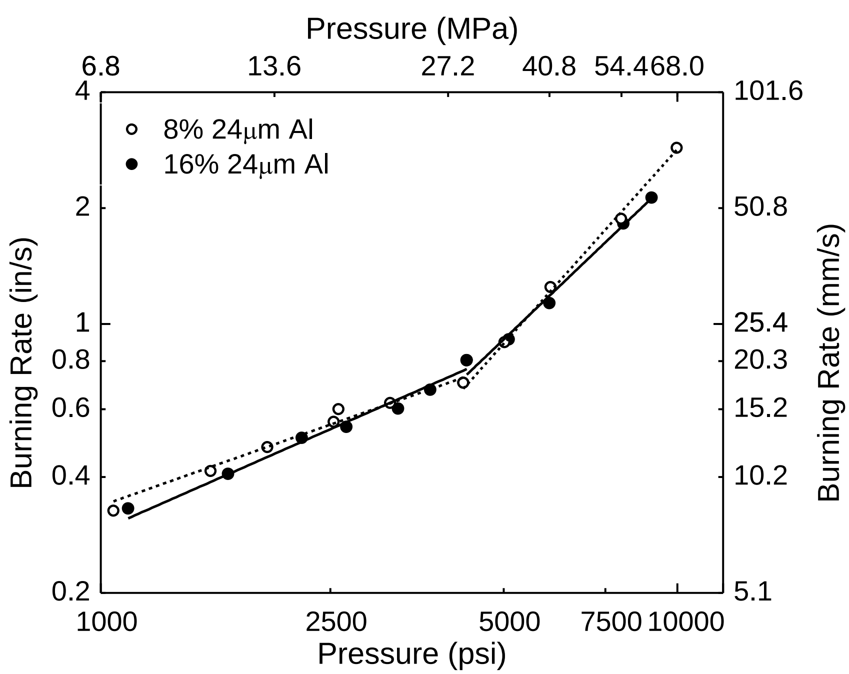

Figure 2. High-pressure burning rate results for 8% and 16%-wt aluminum formulations.

Although few experimental data exist at very-high pressures, several mechanisms have nonetheless been proposed to explain this exponent break feature. The most prominent of these are AP-driven. Irwin, Atwood and Glick et. al. all suggest that above the characteristic pressure, P^*, the contribution of AP to the combustion process dominates, thus the burning rates are controlled by the AP decomposition flame [1,5,13-14]. This hypothesis is supported by Bastress' observation that at higher pressures, the AP surface regresses below the fuel surface [15]. Atwood et. al.'s study also supports this hypothesis since all of the composite propellant formulations tested approached an "AP barrier", the high-pressure exponent region of pure AP, regardless of the AP particle size, modality, micron-aluminum concentration, burning rate catalyst (Fe_2O_3), or plasticizer used [1].

Irwin et. al. further proposed that the increase in burning rates at very-high pressures is due to an increased AP surface area as a result of cracks or pores forming and/or expanding in the AP crystals [5,13]. They later expanded this theory by showing that the most likely cause for the AP cracking is thermal stress induced by the steep temperature gradient in the solid phase at these very-high pressures [13]. An additional theory by Hermance proposed that the pressure exponent increase is a result of the onset of turbulence in the previously laminar fuel-oxidant flame rather than the AP decomposition flame [16-17]. Although each explanation holds merit, further research is required to determine the fundamental mechanism driving the exponent break and resulting characteristic pressure.

4 Conclusion

Overall, aluminized and non-aluminized AP/HTPB-composite propellants were tested at very-high pressures, up to 68.9 MPa (10,000 psi). The new data add to the relatively small database of AP-based propellant burning rates above 20 MPa. All four formulations showed an exponent or "slope" break above 27.6 MPa (4000 psi). The AP distribution did not significantly affect the baseline characteristic pressure or the pressure exponent. Contrastingly, the addition of aluminum lowered the characteristic pressure down from 35.85 MPa (5200 psi) to 29 MPa (4200 psi) compared to the baseline mixtures. The increase in aluminum concentration from 8% to 16% also appeared to lower the pressure exponent, but further testing is required to eliminate the effects of uncertainty in the data analysis. While multiple theories explaining the exponent break phenomena exist, additional very-high pressure burning rate data are required to fully understand the underlying mechanism.

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