AIAA Propulsion and Energy Forum
19-22 August 2019, Indianapolis, IN
AIAA Propulsion and Energy 2019 Forum

10.2514/6.2019-4440

Burning Rate Characterization of Ammonium Perchlorate Pellets Containing Catalytic Additives

Felix A. Rodriguez[1], James C. Thomas[2], Thomas E. Sammet[3], Erica D. Petersen[1], Catherine A. M. Dillier[1], and Eric L. Petersen[4]
Texas A&M University, College Station, TX, 77843, USA

Ammonium perchlorate (AP) is an extensively used oxidizer in solid composite propellants and its combustion behavior can be tailored by the presence of catalytic additives, such as metal oxides. Ammonium perchlorate pellets were manufactured with iron oxide (Fe_2O_3) and titanium oxide (TiO_2) at several mass loadings (0-3% by mass) and burned from 3.45-34.5 MPa (500-5,000 psi) in a constant-volume strand bomb. A Resodyn Acoustic Mixer was utilized to ensure intimate contact between the AP and catalyst additives. The incorporation of 1% Fe_2O_3 yielded the highest burning rate in the investigated pressure region. Irregular burning occurred at lower pressures (< 900 psi) for most formulations which was attributed to radiative heat transfer losses.

I. Introduction

Ammonium perchlorate (AP) is a commonly used oxidizer in solid composite propellants which have a wide range of applications in industries ranging from missile propulsion to space exploration [1]. The inclusion of metal oxides, such as iron oxide (Fe_2O_3) and titania (TiO_2), in composite AP/HTPB propellants has been observed to increase the global burning rates. It is well documented in the literature that metal oxides enhance the thermal decomposition of AP [11]. Wang et al. [2] conducted strand burner experiments with nano-sized CuO, Fe_2O_3 and composite CuO/Fe_2O_3 additives incorporated in composite AP/HTPB propellants, with the Fe_2O_3 formulation increasing the burning rate 66% over the baseline. Stephens et al. [3] utilized a Taguchi L8 matrix to compare multiple parameters in solid composite propellants including additive type, concentration, and size. Their study showed the burning rate had high sensitivity to the additive type, and TiO_2 outperformed CeO_2. Krietz et al. [4] included TiO_2 in composite propellants through several different mixing and preparation methods. Subsequent ballistic testing indicated that intimate contact between the catalyst and other propellant components plays an important role in determining the resultant combustion behavior. More explicitly, the incorporation of TiO_2 showed an increase in burning rate over the corresponding baseline only when intimate contact was achieved. These studies verified that the addition of Fe_2O_3 and TiO_2 have positive effects on the AP/HTPB composite propellant system. Additional investigations of the effect Fe_2O_3 has on reagent and plain AP alone have been conducted previously.

Friedman et al. [5] investigated the deflagration rate of AP pellets pressed from reagent-grade AP of varying particle sizes and preparation methods. The particle sizes utilized therein ranged from a few microns to a few hundred microns, and AP was utilized in the 'as-received' condition and after being sieved to specific size ranges. Pellets (4 × 4 × 38 mm) were manufactured using a hydraulic press (100 ksi) and pellet punch system. The densities of the pellets were seen to deviate from the single-crystal value as the particle size was decreased. The highest density achieved in this study was 1.908 g/cc, which is approximately 97.8% of the single-crystal density. Burning rate data were gathered using a nitrogen-pressurized stand burner coupled with a hot wire ignition system. Several timing fuse wires and

[1] Graduate Researcher, J. Mike Walker '66 Department of Mechanical Engineering, AIAA Student Member.
[2] Postdoctoral Research Associate, J. Mike Walker '66 Department of Mechanical Engineering, AIAA Senior Member
[3] TEES Research Assistant Engineer, J. Mike Walker '66 Department of Mechanical Engineering, AIAA Senior Member
[4] Nelson-Jackson Professor, J. Mike Walker '66 Department of Mechanical Engineering, AIAA Senior Member

motion-picture photography were used to track the flame propagation through the pellets. Testing of the "as received" AP resulted in upper and lower deflagration limits of 45 atm (660 psi) and 300 atm (4400 psi), respectively. Testing completed with the sieved AP resulted in a decreased region of burning rate data, the lower deflagration limit moved to a higher pressure and the upper deflagration limit moved to a lower pressure. The disagreement associated with the sieved and 'as-received' samples was attributed to the lower densities in the sieved AP. Accordingly, the 'as-received' samples were chosen for further testing. Several catalysts were incorporated into the AP pellets at a mass loading of 3%. Fe_2O_3 was found to decrease burning rates at lower pressures and increase burning rates at higher pressures. The crossover point where Fe_2O_3 began to have a positive catalytic effect was approximately 116 atm (1700 psi). The concentration of Fe_2O_3 was not investigated further due to copper chromite formulations yielding the highest burning rate.

Boggs et al. [6] studied the combustion of single-crystal AP and pellets pressed from 99.9% pure AP with particle sizes ranging from 44-77 μm. Pellets (2 × 6 × 10 mm) were manufactured using a hydraulic press which applied a force of 48,600 psi for 30 minutes. Experiments were conducted in a stainless-steel window bomb with pressurization capabilities up to 2,000 psi. A braided nichrome wire was used to achieve sample ignition. Burning rate data were extrapolated using a high-speed camera. This testing methodology was implemented with single-crystal AP samples and resulted in a low degree of scatter. The same low degree of scatter did not translate to the AP with additive-pressed pellet experiments due to nonuniform burning of the additive pellets and not the measurement precision. Additive formulations were manufactured with Fe_2O_3 at 2% and 8% concentration by mass, and the 2% Fe_2O_3 pellets yielded an increase in the deflagration rate and temperature sensitivity of pure AP. The 8% concentration decreased the burning rate and altered the low-pressure deflagration limit to a higher pressure than plain AP. Further experimentation into the optimal percentage of Fe_2O_3 was not conducted.

Marothiya et al. [7] conducted strand burner experiments with AP pellets comparing the effects of mechanically mixed and embedded catalysts. The embedding process consisted of dissolving the AP in water, filtering out any impurities, mixing in the appropriate amount of catalyst, and evaporating the water out slowly, which resulted in catalyst-embedded AP. The process of embedding the AP with catalyst was completed with Fe_2O_3 from several different suppliers. Pellets were shaped into rectangles using a surgical knife, and five of the six faces were inhibited with silica grease. The samples were then burned at 70 bar (~1000 psi) in a Crawford bomb. Fe_2O_3 loading percentages were varied from 0.75-5%. The burning rate of the 1% catalyst loading was the highest, which was reported to agree with the literature. The catalytic effect of Fe_2O_3 decreased as the concentration was increased to 5%. An optimal concertation was found to reside between 0.75 and 1% Fe_2O_3. Multiple suppliers were used for the embedded catalyst samples, and even at the same concentrations different burning rates were observed. This observation alludes to the importance of additive characterization.

In summary, metal oxides have been well established as a burning rate modifier for solid propellant ingredients, but the parameters that control these mechanisms have not been adequately characterized in the literature. In the current study, Fe_2O_3 and TiO_2 were implemented at various loadings in AP pellets to investigate their potential catalytic effects. Details on the experimental procedure are presented in the following section. Burning rate data were collected in a constant-volume strand burner, the results of which are provided after the experimental procedure section. The performance of AP pellets containing various loadings of each catalyst were compared to a pure AP baseline and to each other. Analogous data for AP pellets containing Fe_2O_3 from the literature were utilized for comparison as well. Finally, a description of potential competing mechanisms is discussed.

II. Experimental Procedure

The pure AP (> 99.9%) utilized herein was donated by American Pacific (AMPAC) and has an average particle size of approximately 250 μm. Previous studies completed by Seetharamacharyulu et al. [8] have indicated that the burning rate of AP pellets is independent of the fundamental AP particle size as long as sufficient pressing parameters (force and duration) are implemented such that a high density (> 98% TMD) is achieved. The average density for each formulation evaluated herein is given in Table 1.

Table 1: Formulation details and average measured densities for all samples evaluated herein.

Formulation	Additive	Additive (wt %)	Density (g/cm^3)		
			Theoretical	Actual	%
1	None	-	1.95	1.92	98.5
2	Iron Oxide	0.5	1.96	1.91	97.7
3	Iron Oxide	1	1.96	1.92	97.9
4	Iron Oxide	2	1.97	1.93	98.1
5	Iron Oxide	3	1.99	1.95	98.1
6	Titania	1	1.96	1.92	98.0
7	Titania	2	1.97	1.93	98.2
8	Titania	3	1.98	1.94	98.0

Iron oxide (Fe_2O_3) and titania (TiO_2) were acquired from Firefox Enterprises and Millipore Sigma, respectively. The manufacturer-reported particle size for both catalysts was 325 mesh (< 44 μm). The catalysts were homogenously mixed at varying concentrations from 0.5% to 3% according to established procedures. The appropriate amount of AP and catalyst to create ten pellets (0.5" × 0.5") was measured into a plastic vial and mixed in a Resodyn Acoustic Mixer (RAM) to ensure homogeneity in the mixture. A RAM utilizes acoustic waves and gyration forces to create small mixing zones on the order of 50 μm throughout the mixture. The parameters utilized herein were 75 g with a 2-min mixing time.

Once the catalyst was homogenously mixed into the AP, an appropriate amount was weighed and placed into a pellet punch. The pellet punch is made of heat-treated A10 tool steel and was thoroughly cleaned between each pellet loading. Pellets were manufactured using a programmable Carver M-NE3890 hydraulic press with a maximum force of 50,000 lb_f. A force of 12,000 lb_f and a one-hour dwell time was applied for all pellets manufactured herein. The hydraulic press and a pellet punch schematic are shown in the left and right images of Fig. 1, respectively.

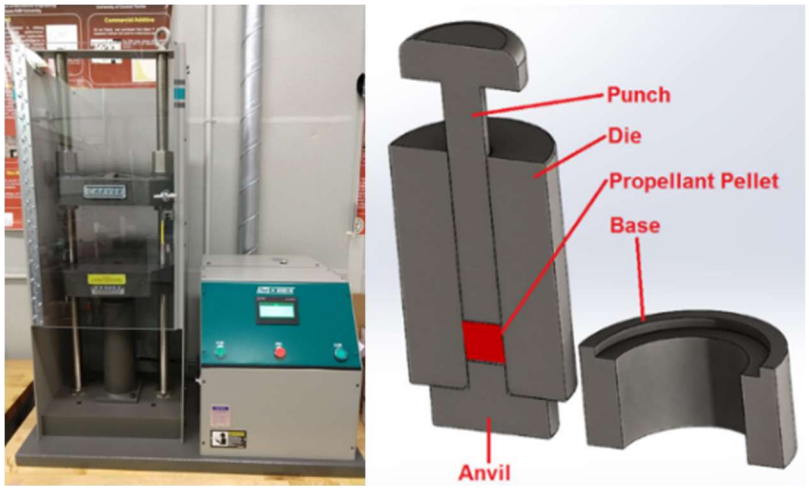

Figure 1: (left) Carver M-NE3890 hydraulic pressed used to manufacture all pellets. (right) A schematic of the pellet punch with an AP/Fe_2O_3 mixture inside.

The mass, m, and length, l, of each pellet were recorded prior to ballistic testing. The parameters were utilized to calculate the pellet density ($\rho = 4m/D^2 l$) and burning rate. The burning rate for a single ballistic experiment is computed as:

$$r = \frac{l}{\Delta t} \tag{1}$$

where Δt is the total pellet burn time which is determined from the transient pressure trace.

Ballistic testing was completed in a constant-volume strand burner at pressures up to 34.5 MPa (5,000 psi). Samples were loaded through the bottom of the strand burner using a custom bolt. Ignition was achieved using a Nichrome wire coupled with an ignitor material (Boron potassium nitrate, $BKNO_3$). An appropriate amount of ignitor material (~0.1 g) was added to the top surface of the pellet over the Nichrome wire. The ignitor material rapidly

combusts upon application of an electrical current to the Nichrome wire and creates a uniform flame above the top surface of the pellet. The flame front subsequently propagates down the length of the pellet in a one-dimensional, steady-state manner. Transient combustion phenomena are monitored with a pressure transducer (OmegaDyne PX02C1-7.5KG), light emission diode (New Focus 2031), UV-VIS spectrometer (Ocean Optics USB2000), and high-speed video (Photron FASTCAM SA3 120K). A schematic of the test setup can be seen in Fig. 2.

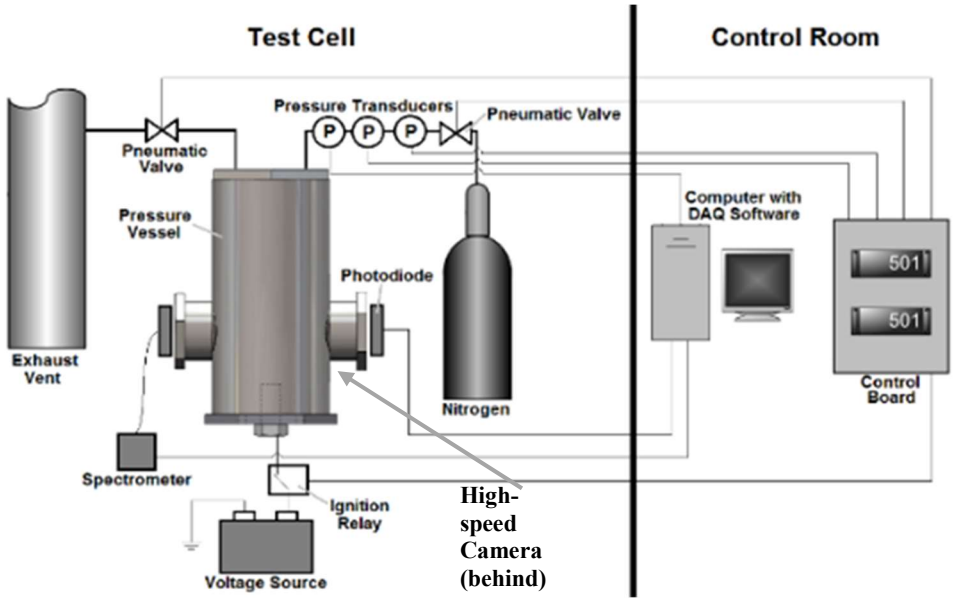

Figure 2: Schematic of the experimental setup employed herein including the constant-volume pressure vessel, ignition system, filling and exhaust system, and control room.

III. Results and Discussion

A baseline ballistic dataset for plain AP without any additives and specific to our test facility has been recently collected by Petersen et al. [9]. Several different sized pellets and pressing parameters (force and time) were explored, along with various ignition methods before the method outlined in the experimental procedure section above was carefully chosen. This method was selected due to production of high pellet densities and maximum reproducibility of burning rate data.

Once the baseline dataset was fully constructed, pellets with Fe_2O_3 and TiO_2 were evaluated. The loading percentage of the catalysts were initially varied from 1-3%. An additional 0.5% Fe_2O_3 formulation was tested to investigate the existence of a catalytic loading and performance threshold. All of the burning rate data collected herein for AP formulations containing TiO_2 or Fe_2O_3 are shown in Fig. 3, along with the corresponding plain AP baseline. The data for formulations containing TiO_2 and Fe_2O_3 are separated in the left and right plots of Fig. 4, respectively, and trend lines are drawn to highlight key trends.

In general, the formulations containing TiO_2 yielded a reduction in the burning rates at lower pressures (< 2,000 psi), but were effective at higher pressures. Furthermore, the formulation containing the least amount of catalyst (1%) exhibited the highest burning rates among the formulations containing TiO_2. It is worth noting that the AP formulation containing 1% TiO_2 was manufactured and tested twice to establish repeatability.

In general, the formulations containing Fe_2O_3 yielded an increase in burning rate across all of the pressures evaluated herein and were more effective at higher pressures. Similar to the trends observed for formulations containing TiO_2, the performance of the propellant decreased as the catalyst loading was incrementally increased from 1% to 3%.

An additional 0.5% Fe_2O_3 formulation was tested to investigate the existence of a catalytic loading and performance threshold. This formulation deviated from the expected trend. In comparison to the formulation containing 1% Fe_2O_3, the burning rate was slightly higher at higher pressures (> 3,000 psi), and the catalytic effect decreased more rapidly at lower pressures. Further testing of the 0.5% Fe_2O_3 formulation at lower pressures is planned.

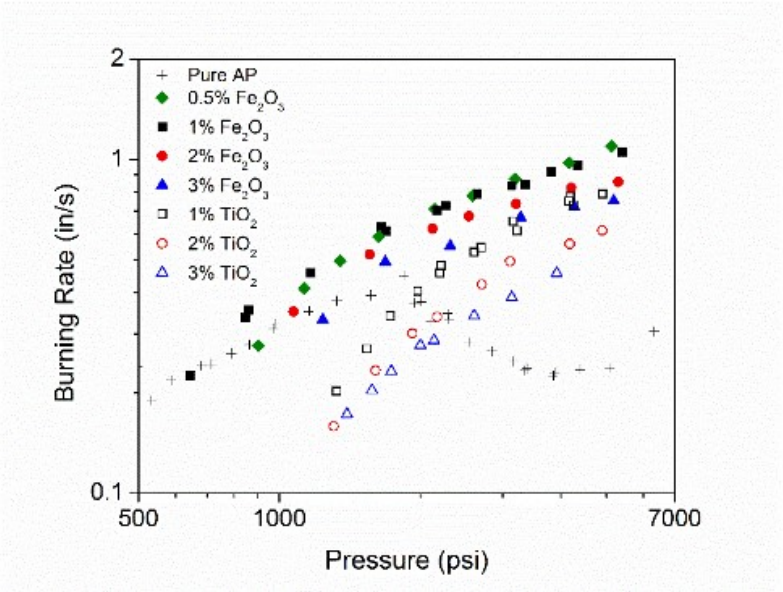

Figure 3: Burning rate data for plain AP pellets and AP pellet formulations loaded with 0.5, 1, 2 and 3% Fe_2O_3 and 1, 2 and 3% TiO_2.

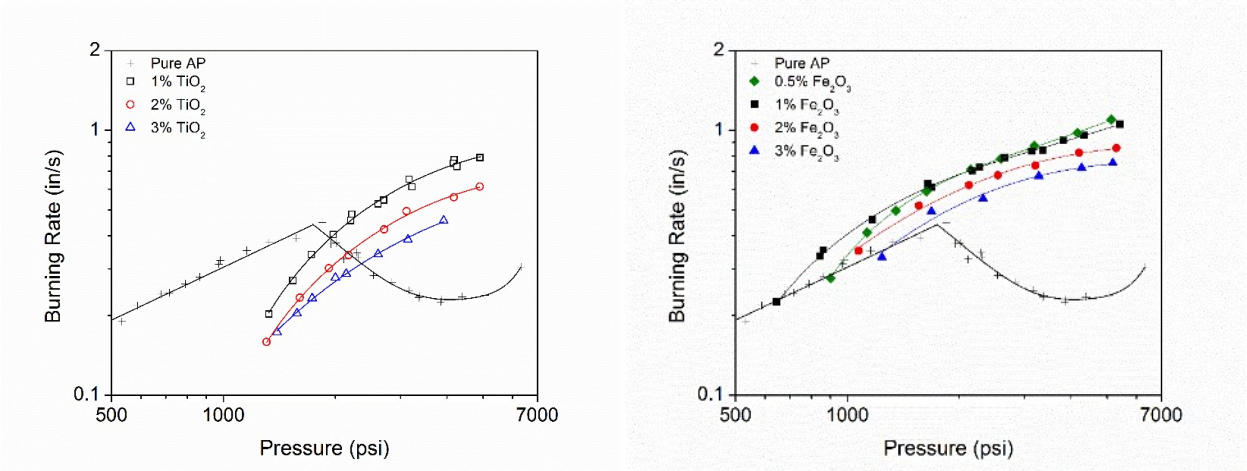

Figure 4: (left) Burning rate data for plain AP pellets and pellet formulations loaded with 1, 2 and 3% TiO_2 with overlaid observed trend lines. (right) Burning rate data for plain AP pellets and pellet formulations loaded with 0.5, 1, 2, and 3% Fe_2O_3 formulations with overlaid trend lines.

Implementation of TiO_2 in AP pellets has not been documented in the open literature, so no comparison of the trends observed herein can be made to previous studies. However, previous studies have been conducted with AP/Fe_2O_3 pellets. The available literature data [5-7] have been compiled and are compared to the current dataset in Fig. 5. The left plot of Fig. 5 compares data for 2% and 3% Fe_2O_3 formulations taken from Boggs et al. [6] and Friedman et al. [5], respectively, with the current dataset. There is good agreement between the current dataset and the data presented by Friedman et al. [5] in terms of general trends and quantitative pellet burning rates. However, there is poor agreement between the data presented by Boggs et al. [5] and the other available data. More explicitly, the data given by Boggs et al. [5] suggest Fe_2O_3 is an effective catalyst in the lower pressure regime, which is in discord with the current dataset and the data presented by Friedman et al. [6]. These observations indicate that the effects of Fe_2O_3 additive on the combustion behavior of AP are dependent on the specific additive characteristics, such as size and geometry, rather than just the chemical composition (i.e., Fe_2O_3). This finding is further supported by the observations made by Morothiya et al. [7] where utilization of Fe_2O_3 from various sources led to significant changes in the catalyst effectiveness in AP pellets. Accordingly, the authors suggest that in all future ballistic studies involving solid propellant ingredients with catalytic additives, that the catalysts be well characterized in terms of their

chemical composition, particle size, geometry, and surface characteristics. Furthermore, the authors are planning on completing a characterization of the metal oxides employed herein by various methods including scanning electron microscopy (SEM) and laser diffraction particle size analyses for a future publication.

The right plot of Fig. 5 compares data for mechanically mixed 0.75-3% Fe_2O_3 formulations taken from Marothiya et al. [7] with the current dataset. Once again, there is good agreement between the two datasets in terms of general trends and quantitative burning rates. Furthermore, the pellet burning rates in both datasets increase with increasing catalyst concentration, and then decrease upon further loading (> 1%). These observations suggest that an optimal catalyst concentration exists for any given catalyst/propellant combination. This trend is related to competing effects during the combustion of catalyst-loaded AP samples. The metal oxides provide a catalytic mechanism which, at most pressures, serves to increase the burning rate of the AP. However, the metal oxides do not react during the combustion process since their melting and vaporization points are higher than the adiabatic flame temperature of the reaction. The metal oxides therefore also soak heat away from the reaction which reduces the flame temperature. The relative dominance of each of these two effects yields an optimal catalyst concentration for maximum burning rate performance, which is dependent on the specific catalytic additive utilized.

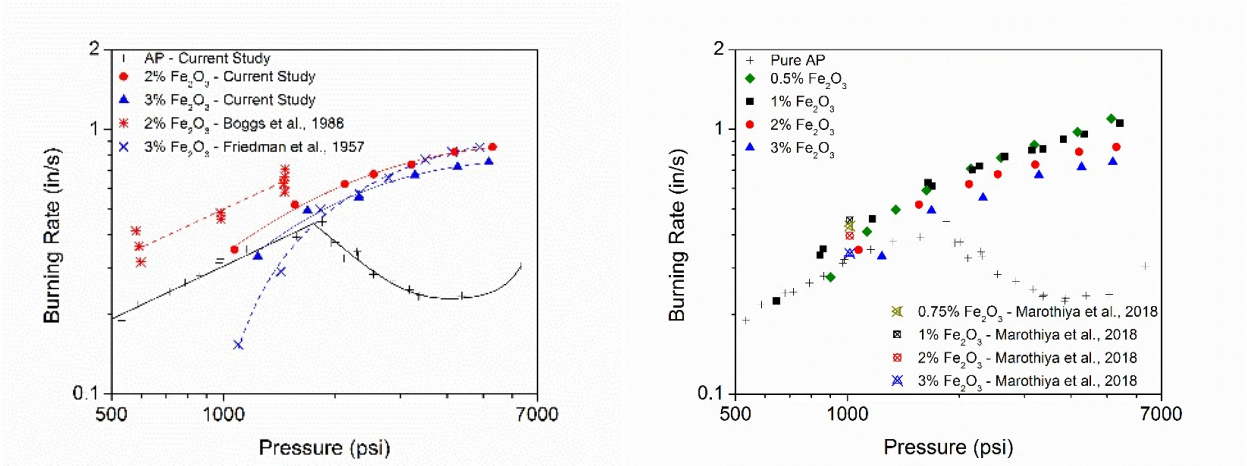

Figure 5: Comparison of literature burning rate data for AP pellets containing Fe_2O_3 to those data collected in the current study. (left) Data taken from Boggs et al. [6] for AP with 2% Fe_2O_3 and Friedman et al. [5] for AP with 3% Fe_2O_3. (right) Data taken from Marothiya et al. [7] for 0.75-3% Fe_2O_3 mechanically mixed with AP.

Additional parameters of importance for AP combustion are the deflagration limits. Testing efforts herein were not concentrated on an in-depth investigation of the lower or upper pressure deflagration limits (LPDL or UPDL) for the examined formulations, but some general trends can be extrapolated from the available data. Neither a LPDL nor an UPDL was established for the baseline, plain AP dataset by Petersen et al. [9] since the authors were able to successfully burn AP as a monopropellant within the experimental testing range (500-5,000 psi).

Testing at lower pressures proved difficult for all formulations containing metal oxide additives. Anomalous pressure traces were consistently collected in the lower-pressure regions (< 1,000 psi). Furthermore, pellet samples had a tendency to quench during the combustion process in the lower-pressure regions. Efforts were not made herein to fully characterize anomalous burning or quenched samples at the lower pressures. The minimum pressure at which anomalous burning occurred generally increased as the catalyst concentration was increased, as can be noted in Fig. 4 by the lowest reported burning rate data for each formulation.

Figure 6 shows representative examples of the pressure traces collected in the lower, middle, and upper pressure regions. The top two pressure traces illustrate representative anomalous burning behavior, and the bottom two pressure traces illustrate normal burning behavior. Anomalous burning behavior was confirmed with high-speed video analysis, where the pellet is generally noted to undergo sporadic combustion prior to quenching. The LPDL of AP is generally associated with radiative heat losses at lower pressures [10]. The metal oxides are not effective burning rate catalysts at lower pressures and also serve to remove heat from the reaction, since they are not reacting. Furthermore, the amount of heat removed from the reacting increases with catalyst concentration. The combination of these observations explains the observed general trend where the LPDL increases to higher pressures as the catalyst concentration is increased.

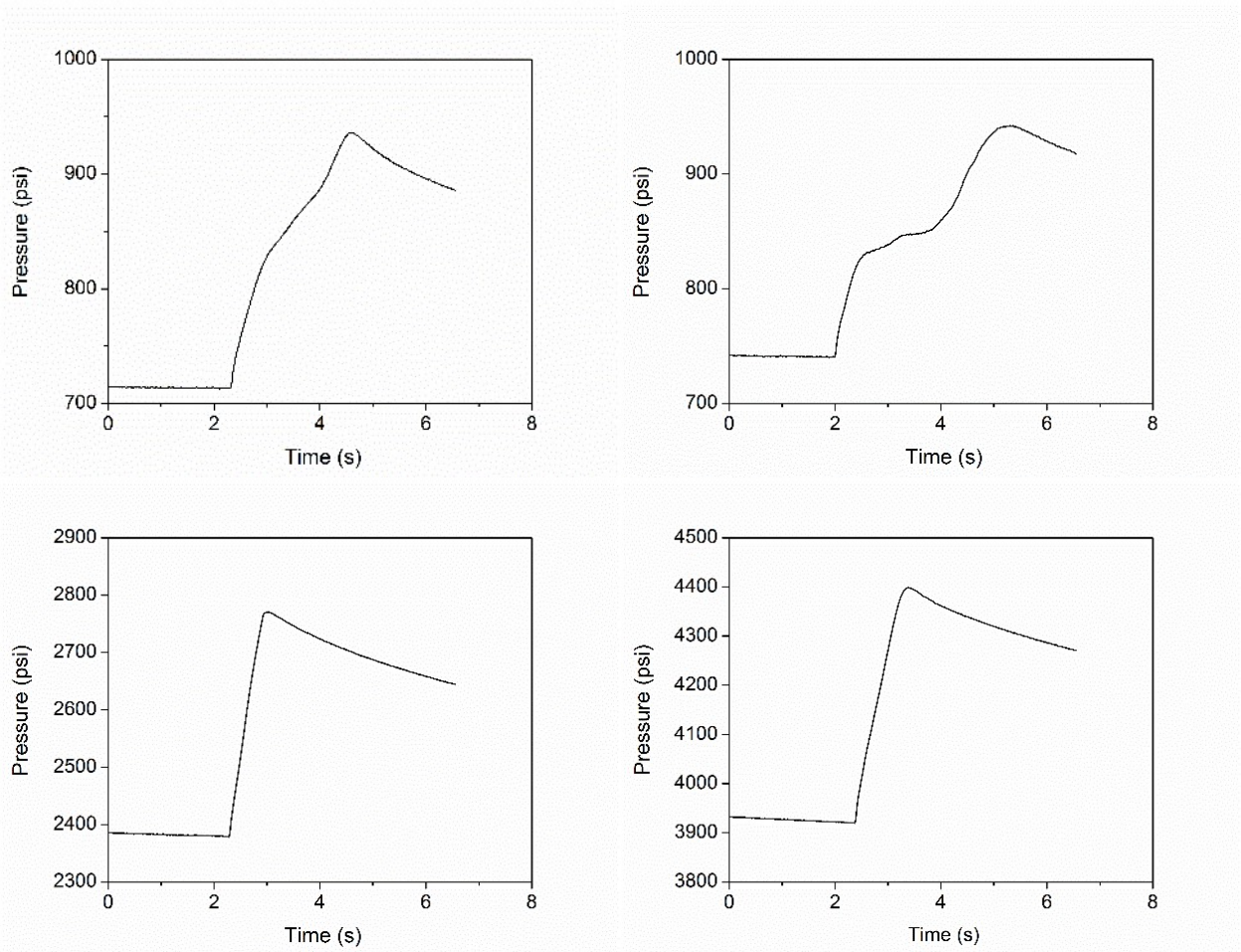

Figure 6: (top, left) Anomalous pressure trace for a 2% Fe_2O_3 formulation at a test pressure of ~800 psi. (top, right) Anomalous pressure trace for a 3% Fe_2O_3 formulation at a test pressure of ~850 psi. (bottom, left) Normal pressure trace for a 1% Fe_2O_3 formulations at a test pressure of ~2,600 psi. (bottom, right) Normal pressure trace for a 2% TiO_2 formulation at a test pressure of ~4,200 psi.

IV. Summary and Conclusions

Catalytic additives were successfully incorporated into plain AP and manufactured into pellets. All (0.5" × 0.5") pellets were tested over a pressure range of 3.45-34.5 MPa (500-5,000 psi). Fe_2O_3 was incorporated at 0.5-3% mass concentrations while TiO_2 was incorporated at 1-3% mass concentrations. The 1% mass loading of both catalysts showed the highest burning rate with respect to like additive concentrations. The 1% Fe_2O_3 formulation showed the highest global burning rate enhancement across all formulations.

In the near future, plans have been made to retest 0.5% Fe_2O_3 samples at lower pressures to obtain clarity with regard to the low-pressure trends. Imaging for all catalysts and formulations will be done to ensure homogenous mixing throughout the pure AP and the fully characterize the catalysts used.

References

[1] Sutton, G.P. and Biblarz, O., *Rocket Propulsion Elements*, 7th ed., Wiley, New York, 2001.

[2] Wang, Y., Xia, X., Zhu, J., Li, Y., Wang, X., and Hu, X., "Catalytic Activity of Nanometer-Sized CuO/Fe_2O_3 on Thermal Decomposition of AP and Combustion of AP-Based Propellants," *Combustion Science and Technology*, 2010, pp. 154-162.

[3] Stephens, M. A., Petersen, E. L., Carro, R., Reid, D. L., Seal, S., "Multi-Parameter Study of Nanoscale TiO_2 and CeO_2 Additives in Composite AP/HTPB Solid Propellants*", Propellants, Explosives, Pyrotechnics*, Vo. 35, 2010.

[4] Kreitz, K., Petersen, E, Reid, D., and Sudipta, S., "Scale-up Effects of Nanoparticle Production on the Burning Rate of Composite Propellant," *Combustion Science and Technology*, Vo. 184, 2012.

[5] Friedman, R., et al., "Deflagration of Ammonium Perchlorate," *Proceedings of the Combustion Institute*, Vol. 6, 1957, pp. 612-618.
[6] Boggs, T. L., et al., "Combustion of Ammonium Perchlorate and Various Inorganic Additives", *J. Propulsion*, Vo. 4, 1988
[7] Mathothiya, G., Vijay, C., Ishitha, K., Ramakrishna, P. A.," An effective method to embed catalyst on AP and its effect on the burn rates of aluminized composite solid propellants," *Combustion and Flame*, Vo. 182, 2017, pp. 114-121.
[8] Seetharamacharyulu, D., Pai Verneker, V. R., and Mallya, R. M., "Defect Sensitization of Combustion and Thermal Decomposition of Ammonium Perchlorate: Effect of Pelletizing Pressure and Dwell Time," *Combustion Science and Technology*, Vol. 28, 1982, pp. 41-53.
[9] Petersen, E. D., Rodriguez, F. A., Dillier, C. A. M., Thomas, J. C., and Petersen, E. L., "Combustion Behavior of Ammonium Perchlorate at High Pressures," These proceedings.
[10] Levy, J. B. and Friedman, R., "Further Studies of Pure Ammonium Perchlorate Deflagration," *Proceedings of the Combustion Institute*, Vol. 8, 1961, pp. 663-672.
[11] Yan, Q., Zhao, F., Kuo, X., Zeman, S., DeLuca, L., "Catalytic effects of nano additives on decomposition and combustion of RDX-, HMX-, and AP-based energetic compositions," *Progress in Energy and Combustion Science*, 2016, pp. 75-136.