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Manufacturing and Temperature Effects on Heat Pellet Ignition Sensitivity

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Abstract: *Reliable ignition of Fe/KClO$_4$ heat pellets is essential for thermal battery performance. Pellet density and exposure to humidity strongly affect heat pellet ignition sensitivity, but other factors may affect performance. Experiments were performed using a 20-Watt 810 nm (IR) solid-state laser in a pulse mode. Pulse width at peak power was varied to adjust energy input. Variables tested include age, surface finish, Fe/KClO$_4$ composition, manufacturer, temperature, and TNT thin film deposition. A 25% increase in ignition energy was observed for a reduction in test temperature from 25°C to -55°C. TNT deposition exacerbated the energy increase at cold temperature but had no effect at room temperature. Significant ignition sensitivity differences were also observed by heat powder manufacturer and pellet pressing technique. The ignition energy was independent of calorific output or burn rate.*

Keywords: ignition sensitivity; heat pellet; thermal batteries; Fe/KClO$_4$; iron/potassium perchlorate.

Introduction

Heat pellets provide the heat source essential for thermal battery activation and performance. Without consistent and predictable heat pellet ignition, thermal battery performance is unreliable. Thus, characterization of heat pellet ignition sensitivity (the energy required to ignite a heat pellet [1]) is critical for the design and development of thermal batteries.

Previous authors have investigated the effects of manufacturing and environmental parameters upon Fe/KClO$_4$ heat pellet burn rate and ignition sensitivity. Increased temperature and decreased particle size increase the burn rate [2]. The burn rate also increases with pellet density, but at a certain point the density becomes so high that combustion is self-quenched and ignition is prevented [2,3]. Rittenhouse shows a significant increase in energy for ignition when heat pellets are exposed to greater than 33% relative humidity for two days, or 42% for 16 hours (at 25°C). Short periods of exposure to higher relative humidity affect pellets more negatively than months of exposure to lower humidity levels [4]. Pellet thickness was not shown to affect burn rate [2]. With respect to ignition sensitivity, exposure to humidity [4], greater pellet density, increased iron particle size, and higher ratios of Fe/KClO$_4$ require increased heat pellet ignition energy [5].

Other important factors that may prevent reliable ignition have not yet been investigated. Laser ignition sensitivity tests were used in this study to measure the energy threshold required for heat pellet ignition. Variables included age, temperature, surface finish, pellet manufacturer, Fe/KClO$_4$ composition, and presence of a TNT thin film.

Experimental Procedures

Table 1 indicates the experimental variables in these tests. Heat pellets consisting of Fe/KClO$_4$ were pressed to a

Table 1. Heat pellet experimental test conditions. Highlighted cells within each column indicate tests to compare.

Type	Powder Year	Fe/KClO$_4$ Composition	Surface Finish	Temperature (°C)	Vendor	TNT film
A	1972	88/12	pristine	25	A	N
B	1979	86/14	pristine	25	A	N
C	1984	88/12	pristine	25	A	N
D	1991	86/14	pristine	25	A	N
E1, E2	1999	88/12	pristine	25	A	N
F	2007	88/12	pristine	25	A	N
G1, G2	1999	88/12	pristine	-55	A	N
H	1999	88/12	pristine	75	A	N
I	1999	88/12	pristine	25	A	Y
J	1999	88/12	pristine	-55	A	Y
K	Unknown	88/12	pristine	25	B	N
L	Unknown	88/12	carbon paint	25	B	N

constant density of 3.35 g/cc. Heat powder was supplied by two commercial vendors (A and B) and manufactured over a span of nearly four decades. All pellet types were manually pressed except for type F, which were pressed on automated systems. $Fe/KClO_4$ ratios in the heat powders included 86/14 and 88/12.

Pellet types E, G, H, K, and J were pressed into pellets from the same powder, but at different times. Types E1, G1, and H were pressed into pellets in 2011. Types E2, G2, I, and J were pressed in 2013. Types E1 and E2 served as the 88/12 reference materials.

Reference 88/12 material was used to determine if the emissivity of the heat pellets has a significant impact on ignition sensitivity. Reference heat pellets were painted with carbon spray and tested for surface finish comparison.

Thin TNT films of 14-20 µm thickness were deposited onto one side of pellet types I and J using an evaporation system. IR measurements confirmed that no TNT was present on the backside of these pellets despite the high porosity of heat pellets.

All heat pellets were stored in a dry room, a laboratory with a very low, well-controlled humidity level. Pellets were moved individually from the dry room prior to testing to minimize exposure to ambient humidity levels.

Ignition sensitivity tests were performed with a 20-Watt 810 nm (IR) solid-state laser in pulse mode. The laser was built by Quantic Industries, Inc. Pulse width at peak power was varied to adjust energy output, where pulses varied from 100 to 700 ms. The pulse amplitude range was maintained at 0 to 5 V. The laser spot size was 2 to 3 mm. The laser was calibrated before, after, and periodically between tests using an Ophir calorimeter. The glass window of the microscope stage cover was integrated during calibration to maintain the same optical path used during testing. Linear calibration curves were calculated to determine the relationship between pulse width and output energy in Joules.

Samples were placed in an airtight, temperature-controlled microscope stage with fine X and Y plane control. The X and Y knobs adjusted the sample position after each pulse to ensure adequate spacing between each pulse. No spot was hit more than once. A liquid nitrogen cooled microscope stage was used to control the heat pellet temperature. Samples were maintained within 1°C of either 25°C, -55°C, or 75°C during testing. Pellets tested at -55°C were placed in the sample stage at room temperature, and the stage was cooled only after samples were sealed inside to protect them from water condensation. Following ignition of each pellet, the stage was returned to room temperature and opened for sample removal. The glass window of the sample stage was cleaned between ignitions.

A modified Bruceton method was applied to determine the correct pulse width for each pulse. The first pulse's energy for each pellet type was very low (i.e. 200 ms pulse width) and increased with a uniform 25 ms step size until ignition occurred. The first pulse of subsequent pellets of the same type was three steps lower than the previous ignition (75 ms lower). Again, each pulse thereafter increased with a uniform 25 ms step size until ignition occurred. The result of each pulse was recorded as either a 0 (no ignition) or a 1 (ignition). A minimum of ten pellets of each type were tested. These results and the calibration data were then analyzed to determine the ignition sensitivity of each pellet type.

Results and Discussion

Periodic sensitivity tests of type E pellets established the baseline ignition sensitivity. The mean ignition energy for E1 pellets was 5.1±0.9 J, averaged over five tests with a ±95% confidence interval (Figure 1). Anomalous tests on 7/30/13 indicated lower ignition energy, possibly due to temporary use of a different pulse generator. With those results excluded, the mean ignition energy was 5.4±0.6 J. The mean ignition energy for E2 pellets was similar, 5.7±0.6 J, averaged over 3 tests. Since both averages are within one standard deviation of each other, the ignition sensitivity baseline data compares well to pellets pressed from the same powder at different times. It also supports consistent laser output energy over time. However, previous tests performed on similar equipment show an ignition sensitivity of 1 to 3 J. This is substantially lower than the energy levels reported here. The setup used here was from a previous system and was modified prior to testing for the addition of temperature control. It is believed that the laser system was slightly defocused during modification. Though the consistent post-modification results indicate quantitative comparisons are possible, the absolute values are not directly comparable to other testing techniques, such as static sensitivity testing.

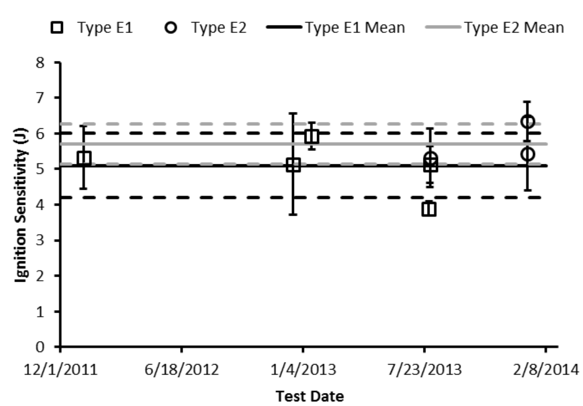

Figure 1. Baseline ignition sensitivity of type E pellets.

Pellets were tested to ensure the laser energy was effectively absorbed. Pellets with carbon paint ignited at 7.5±1.0 J, compared to 7.1±1.4 J for unpainted, pristine pellets (from a different lot than the baseline pellets). This indicates that laser energy absorption is excellent in the untreated pellets and justifies the use of plain pellets in the laser system.

Supplier variability was tested by comparing results from pellet types E1 and K. Comparison demonstrates a substantial difference in ignition sensitivity for pellets, which were pressed by two different vendors, but in the same manner. Pellets from Vendor B required a mean 7.1±1.4 J, whereas the reference E1 pellets from Vendor A required a mean 5.1±0.9 J, nearly 40% less energy. Though the specific differences between these powders and pellets have not yet been investigated, Guidotti et al., reported that manufacturing differences such as iron particle size can strongly affect ignition sensitivity [5].

The effect of temperature upon mean ignition sensitivity revealed a 25% increase for pellets tested at -55°C (7.5±0.2 J) when compared to tests conducted at 25°C (5.9±0.3 J) and 75°C (5.7±0.5 J). Tests at 75°C required slightly less energy than tests at 25°C, but this difference was not statistically significant, as seen in Figure 2. This indicates that at lower temperatures, ignition sensitivity may depend on the competition between self-quenching, caused by cooling, and flame propagation, similar to the observation made by both Reed et al., and McCarthy et al. [2,3].

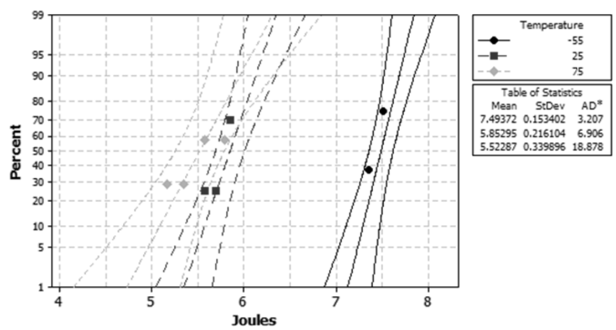

Figure 2. Probability plot for energy threshold showing the effect of temperature on ignition sensitivity.

TNT may have been present on heat pellets exposed to certain primer compositions for long periods of time [6]. TNT deposition on heat pellets required a slight increase in ignition energy compared to identical control pellets for tests conducted at 25°C, for which the ignition sensitivity was measured to be 6.3±2.0 J versus 5.6±1.8 J, respectively. At -55°C, however, the difference was significant. Control pellets ignited at 8.3±1.5 J, but because only one of ten heat pellets with TNT ignited, no mean ignition sensitivity could be established for comparison. Each pellet that failed to ignite was tested at the maximum pulse width three times in three different spots. Because this energy output tested the limits of our laser, either the maximum energy output for the laser was just slightly below the ignition sensitivity of these pellets, or at cold temperatures, the effects of TNT deposition compete with heat pellet burn front propagation. The reasons for this outcome have yet to be established.

No observable trend occurred from differences in $Fe/KClO_4$ composition. 86/14 and 88/12 heat pellets were tested. This indicates $Fe/KClO_4$ composition and ignition sensitivity are not related, which is contrary to results reported by Guidotti et al. [5], although the correlation found by Guidotti was weak. A lack of correlation is expected because ignition is dependent upon local effects between iron and potassium perchlorate. This chemical reaction requires the same activation energy independent of the overall composition, and once activated, quenching is unlikely.

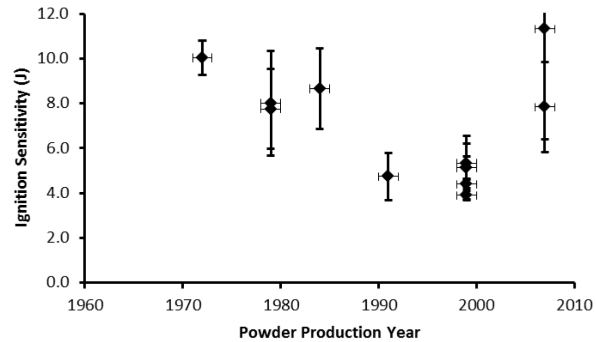

Figure 3. Aging effects upon ignition sensitivity.

Pellet types A through F were extracted from thermal batteries fabricated between 1972 and 2007. All pellets were fabricated from heat powder made by the same manufacturer. Figure 3 shows what appears to be a nearly linear trend between powder production year and ignition energy. This suggests a previously unsuspected aging trend in heat pellets. It is possible to speculate as to the source of such an aging trend, but more data is necessary to confirm this unexpected result.

The pellets from 2007 did not follow the apparent aging trend, however, as they required greater energy to ignite and also demonstrated greater variability. The 2007 pellets

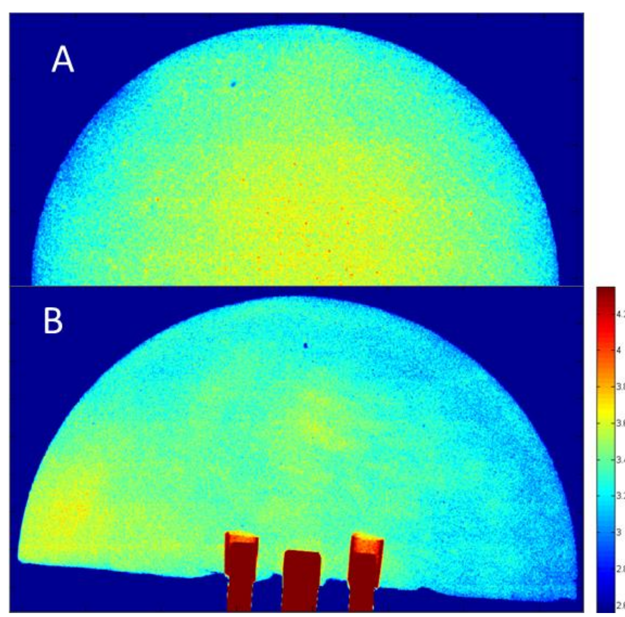

Figure 4. Local density comparisons between (A) manual and (B) automated pellet pressing processes.

do not dismiss the aging hypothesis because manufacturing effects may explain the difference. Automated presses were employed to create the 2007 pellets, while manual presses were used to form all the earlier pellets. The spot size of the laser system is less than 3 mm. Local density variation was measured using an X-ray system calibrated with a density standard. The results (Figure 4) show the local density varies from approximately 3.1 to 3.9 g/cc, even with a nominal pellet density. This is a significant density variation. Previous ignition sensitivity efforts suggest that the highest density areas may require two times more energy to ignite than the optimal density area [7].

The magnitude of density variation is larger in automated presses and the form is different. The automated presses show signs of powder clumping and tend to have higher density on one side than the other, as might be expected from a single sweeping action to smooth the powder in the die. Manually pressed pellets tend to be more homogenous, but with lower density around edges. This is consistent with loading in the center of the die and spreading to the edges.

Conclusions

Systematic testing of vendor, temperature, TNT deposition, age, $Fe/KClO_4$ composition, and surface finish, demonstrated parameters that can significantly affect heat pellet ignition sensitivity. Little or no observable effects resulted from changes to surface finish, composition, or coating with TNT at ambient temperature. Ignition sensitivity was substantially affected by cold temperature. This sensitivity was heightened with TNT coating. Manufacturing effects are also important for ignition sensitivity. Specifically, differences across powder vendors and pressing modes (manual vs. automated) were observed. Finally, the present work suggests a previously unidentified aging trend that will be explored in future work.

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